This is a digital copy of a book that was preserved for generations on library shelves before it was carefully scanned by Google as part of a project to make the world's books discoverable online.

It has survived long enough for the copyright to expire and the book to enter the public domain. A public domain book is one that was never subject to copyright or whose legal copyright term has expired. Whether a book is in the public domain may vary country to country. Public domain books are our gateways to the past, representing a wealth of history, culture and knowledge that's often difficult to discover.

Marks, notations and other marginalia present in the original volume will appear in this file - a reminder of this book's long journey from the publisher to a library and finally to you.

Usage guidelines

Google is proud to partner with libraries to digitize public domain materials and make them widely accessible. Public domain books belong to the public and we are merely their custodians. Nevertheless, this work is expensive, so in order to keep providing this resource, we have taken steps to prevent abuse by commercial parties, including placing technical restrictions on automated querying.

We also ask that you:

+ *Make non-commercial use of the files* We designed Google Book Search for use by individuals, and we request that you use these files for personal, non-commercial purposes.
+ *Refrain from automated querying* Do not send automated queries of any sort to Google's system: If you are conducting research on machine translation, optical character recognition or other areas where access to a large amount of text is helpful, please contact us. We encourage the use of public domain materials for these purposes and may be able to help.
+ *Maintain attribution* The Google "watermark" you see on each file is essential for informing people about this project and helping them find additional materials through Google Book Search. Please do not remove it.
+ *Keep it legal* Whatever your use, remember that you are responsible for ensuring that what you are doing is legal. Do not assume that just because we believe a book is in the public domain for users in the United States, that the work is also in the public domain for users in other countries. Whether a book is still in copyright varies from country to country, and we can't offer guidance on whether any specific use of any specific book is allowed. Please do not assume that a book's appearance in Google Book Search means it can be used in any manner anywhere in the world. Copyright infringement liability can be quite severe.

About Google Book Search

Google's mission is to organize the world's information and to make it universally accessible and useful. Google Book Search helps readers discover the world's books while helping authors and publishers reach new audiences. You can search through the full text of this book on the web at `http://books.google.com/`

1837
ARTES VERITAS SCIENTIA
LIBRARY OF THE
UNIVERSITY OF MICHIGAN
E PLURIBUS UNUM
TUEBOR
SI QUAERIS PENINSULAM AMOENAM CIRCUMSPICE
IN MATHEMATICS
[redacted]
LIBRARY

THE GIFT OF
MRS. JOHN OREN REED

Mathematics
QC
311
.A38

TREATISE

ON

THERMODYNAMICS

BY

PETER ALEXANDER, M.A.

Ex-Breadalbane Scholar, Glasgow University;

Lecturer on Mathematics, Queen Margaret College, Glasgow

LONDON

LONGMANS, GREEN, AND CO.

AND NEW YORK: 15 EAST 16th STREET

1892

DUBLIN:
PRINTED AT THE UNIVERSITY PRESS,
BY PONSONBY AND WELDRICK.

Math Lit
Gift
Mrs. J. O Reed
4-12-33

04-17-38 MEW

PREFACE.

THIS TREATISE is a new development of all the details of the subject directly from the two laws, and thus exhibits the science as *an organic unity*, instead of so many *detached propositions* developed *from mathematical rather than physical considerations*. This is done by first obtaining mathematical expressions of the two laws in *general* forms applicable to *any elementary cycle*, and then from these general forms deriving the particular forms characteristic of the particular elementary cycles. When this has been done, the whole system of mathematical formulæ embodying the details of the science has been obtained. All this is first exhibited in forms in terms of *any* scale of temperatures, and is afterwards transformed into forms in terms of the *absolute* scale.

In Chapter VI. is exhibited for the first time (as far as I am aware) the *general extension of the Second Law* in terms of *any* scale of temperatures, and equation (39) exhibits Carnot's Function *in a new form much more general than any hitherto given*, which is derived from the said general extension of the Second Law.

Chapters X. and XI. are specially interesting, showing as they do that the absolute scale of temperatures *is often*

mis-defined, and that, if the specific heat of air under constant pressure *has a constant value* (or rather *does not vary with p*), *the numbers on the absolute scale either do not differ from the corresponding numbers on the scale of the constant-pressure air thermometer, or differ from them by a quantity which is the* SAME THROUGHOUT THE SCALES. It is also shown that the result derived by Joule and Thomson, from their experiments on the flow of gases through porous plugs, *is inconsistent with the constancy or even slow variation* of the specific heats of gases under constant pressures.

In Chapter XVI. the fog that has up till now hung over the subject of reversibility and irreversibility is cleared away by introducing the *new notions* of *intrinsic irreversibility* and *conditional irreversibility*, and by showing that no transformation is really (*i.e.* intrinsically) irreversible, during which the body undergoing transformation has at every instant the same pressure and temperature throughout all its parts.

Chapters XVI. and XVII. also clear away some haziness from the subjects of Motivity and Dissipation of Energy by pointing out that, when the integral $\int \frac{dH}{t}$ is spoken of as having zero value for reversible cycles, and negative values for irreversible cycles, t does not denote the temperature of the working body, but that of the external body from which it is receiving heat, or to which it is imparting heat. On the other hand, it is shown that, if t denote *the temperature* (*throughout*) *of the working body*, $\int \frac{dH}{t}$ is *always* zero for a cycle.

Chapter XVIII. extends *the ordinary definition of entropy to a body or system in which the temperature or pressure, or both, are not the same throughout the body or system, and thus opens up a mode of dealing with intrinsically irreversible transformations the same as that followed when the transformations are reversible.*

Throughout these pages the principle of the "Conservation of Energy" has been *tacitly assumed*, and terms whose meanings are supposed to be generally understood have not been defined. To remedy this a list of definitions is prefixed. Also, except in Chapter XV., entropy is supposed to be numbered so that the addition of $\frac{\tau}{J}$ units of heat to unit mass of a substance of temperature τ causes its entropy to increase by unity. This has been done to secure the advantage of having the diagram divided into equal areas, *each representing a unit of work*, by a network of isotherms and isenergs numbered by two arithmetical series *whose common difference is unity*. In Chapter XV. the isentropes are numbered, so that the addition of τ units of heat to unit mass of a substance of temperature τ causes its entropy to increase by unity. This has been done for the purpose of obtaining the equations in the *usual forms*.

QUEEN MARGARET COLLEGE, GLASGOW,
September, 1892.

CONTENTS.

Chapter.		Page.
I.	FORMULÆ OF TRANSFORMATION,	1
II.	ON THE GEOMETRICAL REPRESENTATION OF WORK,	6
III.	A SHORT HISTORY OF THERMODYNAMICS,	16
IV.	THE TWO LAWS OF THERMODYNAMICS,	29
V.	THERMAL LINES AND CYCLIC DIAGRAMS,	38
VI.	EXTENSION OF THE SECOND LAW,	46
VII.	ALGEBRAIC EXPRESSIONS FOR VARIOUS CYCLES,	51
VIII.	VALUES OF PARTIAL DIFFERENTIAL COEFFICIENTS,	63
IX.	COEFFICIENTS OF ELASTICITY AND DILATATION,	74
X.	ABSOLUTE SCALE OF TEMPERATURES,	81
XI.	RELATION OF THE ABSOLUTE SCALE TO THE SCALE OF THE CONSTANT-PRESSURE AIR THERMOMETER,	88
XII.	PERFECT GASES,	97
XIII.	VAPOURS NOT IN CONTACT WITH THEIR LIQUIDS,	110
XIV.	LATENT HEAT,	122
XV.	USUAL METHOD OF OBTAINING THERMODYNAMIC FORMULÆ,	150
XVI.	REVERSIBILITY AND IRREVERSIBILITY,	173
XVII.	THERMODYNAMIC MOTIVITY AND DISSIPATION,	179
XVIII.	ON THE ENTROPY, ETC., OF A BODY OR SYSTEM OF BODIES WHOSE TEMPERATURE AND PRESSURE ARE NOT THE SAME AT ALL PARTS OF THE BODY OR SYSTEM,	187
	EXERCISES,	195

INTRODUCTION.

In starting to write this Treatise I intended to produce a pamphlet which would be useful to students wishing to graduate with honours; but, on attempting to simplify Thomson's proof of his extension of the Second Law, I was led to consider whether the extension could not be made *generally* for *any* scale of temperatures (Thomson's extension only holding for the absolute scale), and found it could be. Having accomplished this, I next considered whether the two laws could not be expressed in terms of other elementary cycles than Carnot's, and found that they could be. I then determined to begin anew and remodel the whole subject on the following plan:—

(1). Starting from the two laws as usually stated in terms of Carnot's Cycle to extend them to *any cycle*, and in terms of *any scale of temperatures.*

(2). To apply these extensions to *any elementary cycle* represented by a figure enclosed by two pairs of thermal lines—one pair of one kind, and another pair of another kind.

(3). From (2) to develop the whole subject by choosing the two pairs of lines, so as to represent all the usual elementary cycles.

(4). To introduce Thomson's Absolute Scale of Temperatures.

(5). To consider the subject of reversibility; and, if possible, put it in a clearer light, as it seemed to be rather foggy.

(6). To conclude with the subject of Motivity and Dissipation of Energy, which also needed clearing up.

In considering the Absolute Scale, I found that a misleading definition is sometimes given of absolute temperature, namely, that it is *the reciprocal of Carnot's Function.* This definition is either *untrue*, or else it is *a loose statement* of the following:—

Absolute temperature is a number denoting the temperature of a body on a scale of temperatures which is such that, if Carnot's Function corresponding to this temperature be expressed numerically in terms of this scale, these two numbers will be mutually reciprocal.

I found also that the existing expositions of the relation between the Absolute Scale and the Scales of the Constant-pressure and Constant-volume Air Thermometers were *far from satisfactory.* On trying to remedy this I found that, if the specific heats of air be constant, the numbers on the Absolute Scale *will either not differ from those on these two scales, or will differ from them by the same quantity throughout.*

I have thus reduced the subject to *an organic unity, having developed the whole directly from the two laws,* thus removing the reproach that after stating the two laws, little use is made of them, the details being seemingly derived *from mathematical rather than physical principles.*

I have used the following Definitions of Terms throughout the Treatise:—

Principle of Conservation of Energy.—Energy is uncreatable and indestructible, but may be transferred from one

body to another, or may be transmuted from one form into another; a certain quantity of the one form being equivalent to a certain other quantity of the other form.

Specific heat of a substance = the quantity of heat which will raise by one degree the temperature of unit mass of the substance. There are two principal varieties of this, indicated by K or $\left(\frac{dH}{dt}\right)_p$ and N or $\left(\frac{dH}{dt}\right)_v$, the former being the specific heat of the substance when its pressure remains unchanged, and the latter the specific heat of the substance when its volume remains unchanged. There are other varieties of specific heat.

$\left(\frac{dH}{dx}\right)_t = \lambda$ = *latent heat* of a form of a substance, that is, the quantity of heat which unit mass of this form of the substance will evolve while changing from this form to the next lower form without changing its temperature. There are two varieties of this, namely, "*latent heat of fusion or liquefaction*," and "*latent heat of evaporation*," meaning respectively the quantity of heat evolved by unit mass of the liquid form during solidification unattended by change of temperature, and the quantity evolved by unit mass in the vapour form during liquefaction without change of temperature.

$M = \left(\frac{dH}{dv}\right)_t$ = *latent heat of dilatation*, that is, the quantity of heat absorbed by unit mass of a body per unit increase of its volume while its temperature remains unchanged.

E = *Energy*, or *Intrinsic energy* of a substance, is the total capacity for doing work of unit mass of the substance. When the substance parts with heat, or does external work, its energy diminishes; but when heat is added to it, or work is done upon it, its energy increases.

ϕ = entropy of a substance is that property of the substance whose numerical value increases or diminishes when heat is communicated to or taken from the substance respectively, but remains unchanged when no heat is added to or taken from the substance.

t = temperature of a body is its state with respect to *sensible* heat, or it is the measure of its tendency to communicate heat to other bodies. Absolute zero of temperature is the temperature corresponding to total deprivation of heat. It is 273° or 274° C. below the freezing temperature.

Boyle's Law for gases is that for a given mass of the gas $p \cdot v$ remains constant so long as its temperature remains constant.

Charles' Law for gases is that for a given mass of the gas $\frac{v}{t}$ remains constant so long as its pressure remains constant. A gas is said to be perfect when it perfectly obeys these laws.

V = specific volume of a substance in a given form is the volume of unit mass of that form of the substance.

THERMODYNAMICS.

CHAPTER I.

FORMULÆ OF TRANSFORMATION.

As certain purely mathematical formulæ of transformation

Beginners should read this work in the following order :—

Chapters III., IV., II., I. (Geometrical portion, pages 4 and 5), V., VI., VII., IX., XII., X. (pages 81 and 82), XIII., XIV.

$$\delta z = \left(\frac{dz}{dx}\right)_y \delta x + \left(\frac{dz}{dy}\right)_x \delta y.$$

Hence, if $\delta z = 0$,

$$0 = \left(\frac{dz}{dx}\right)_y \delta x + \left(\frac{dz}{dy}\right)_x \delta y;$$

$$\therefore \quad \frac{\left(\frac{dz}{dx}\right)_y}{\left(\frac{dz}{dy}\right)_x} = -\left(\frac{\delta y}{\delta x}\right)_z = -\left(\frac{dy}{dx}\right)_z \qquad (1)$$

Again, if x, y, α, and β be variables, so related that the values of any two being known the values of the others follow, it can be proved that

$$\left(\frac{dx}{dy}\right)_\alpha \cdot \left(\frac{dy}{dx}\right)_\beta = \left(\frac{d\alpha}{d\beta}\right)_x \cdot \left(\frac{d\beta}{d\alpha}\right)_y. \tag{2}$$

This may be proved thus :—

$$\left(\frac{dx}{dy}\right)_\alpha \cdot \left(\frac{dy}{dx}\right)_\beta = \left[-\frac{\left(\frac{d\alpha}{dy}\right)_x}{\left(\frac{d\alpha}{dx}\right)_y}\right] \cdot \left[-\frac{\left(\frac{d\beta}{dx}\right)_y}{\left(\frac{d\beta}{dy}\right)_x}\right] \quad \text{from (1)}$$

$$= \frac{\left(\frac{d\alpha}{dy}\right)_x}{\left(\frac{d\beta}{dy}\right)_x} \cdot \frac{\left(\frac{d\beta}{dx}\right)_y}{\left(\frac{d\alpha}{dx}\right)_y}$$

$$= \left(\frac{d\alpha}{d\beta}\right)_x \cdot \left(\frac{d\beta}{d\alpha}\right)_y. \tag{2}$$

Again, the same quantities being similarly related,

$$\frac{\left(\frac{dx}{d\alpha}\right)_y}{\left(\frac{dx}{d\beta}\right)_y} = \left(\frac{d\beta}{d\alpha}\right)_y$$

$$= -\frac{\left(\frac{dy}{d\alpha}\right)_\beta}{\left(\frac{dy}{d\beta}\right)_\alpha} \quad \text{from (1);}$$

$$\therefore \left(\frac{dx}{d\alpha}\right)_y \cdot \left(\frac{dy}{d\beta}\right)_\alpha = -\left(\frac{dx}{d\beta}\right)_y \cdot \left(\frac{dy}{d\alpha}\right)_\beta.$$

Similarly, or by interchanging x and y,

$$\left(\frac{dy}{d\alpha}\right)_x \left(\frac{dx}{d\beta}\right)_\alpha = -\left(\frac{dy}{d\beta}\right)_x \cdot \left(\frac{dx}{d\alpha}\right)_\beta.$$

Also, by interchanging y and β in (2),

$$\left(\frac{dx}{d\beta}\right)_\alpha \cdot \left(\frac{d\beta}{dx}\right)_y = \left(\frac{d\alpha}{dy}\right)_x \cdot \left(\frac{dy}{d\alpha}\right)_\beta;$$

$$\therefore \quad \left(\frac{dx}{d\beta}\right)_\alpha \cdot \left(\frac{dy}{d\alpha}\right)_x = \left(\frac{dx}{d\beta}\right)_y \cdot \left(\frac{dy}{d\alpha}\right)_\beta.$$

Also,

$$\left(\frac{dx}{d\alpha}\right)_y = \left(\frac{dx}{d\alpha}\right)_\beta + \left(\frac{dx}{d\beta}\right)_\alpha \cdot \left(\frac{d\beta}{d\alpha}\right)_y$$

$$= \left(\frac{dx}{d\alpha}\right)_\beta - \left(\frac{dx}{d\beta}\right)_\alpha \cdot \frac{\left(\frac{dy}{d\alpha}\right)_\beta}{\left(\frac{dy}{d\beta}\right)_\alpha} \text{ from (1)}$$

$$= \left(\frac{dx}{d\alpha}\right)_\beta - \left(\frac{dx}{dy}\right)_\alpha \cdot \left(\frac{dy}{d\alpha}\right)_\beta;$$

$$\therefore \quad \left(\frac{dx}{d\alpha}\right)_y \cdot \left(\frac{dy}{d\beta}\right)_\alpha = \left(\frac{dx}{d\alpha}\right)_\beta \cdot \left(\frac{dy}{d\beta}\right)_\alpha - \left(\frac{dx}{dy}\right)_\alpha \cdot \left(\frac{dy}{d\alpha}\right)_\beta \cdot \left(\frac{dy}{d\beta}\right)_\alpha$$

$$= \left(\frac{dx}{d\alpha}\right)_\beta \cdot \left(\frac{dy}{d\beta}\right)_\alpha - \left(\frac{dx}{d\beta}\right)_\alpha \cdot \left(\frac{dy}{d\alpha}\right)_\beta.$$

Wherefore, collecting the last four results,

$$\left.\begin{aligned}
\left(\frac{dx}{d\alpha}\right)_\beta \cdot \left(\frac{dy}{d\beta}\right)_\alpha - \left(\frac{dx}{d\beta}\right)_\alpha \cdot \left(\frac{dy}{d\alpha}\right)_\beta &= \left(\frac{dx}{d\alpha}\right)_y \cdot \left(\frac{dy}{d\beta}\right)_\alpha \\
&= -\left(\frac{dx}{d\beta}\right)_y \cdot \left(\frac{dy}{d\alpha}\right)_\beta \\
&= -\left(\frac{dx}{d\beta}\right)_\alpha \cdot \left(\frac{dy}{d\alpha}\right)_x \\
&= \left(\frac{dx}{d\alpha}\right)_\beta \cdot \left(\frac{dy}{d\beta}\right)_x
\end{aligned}\right\}. \quad (3)$$

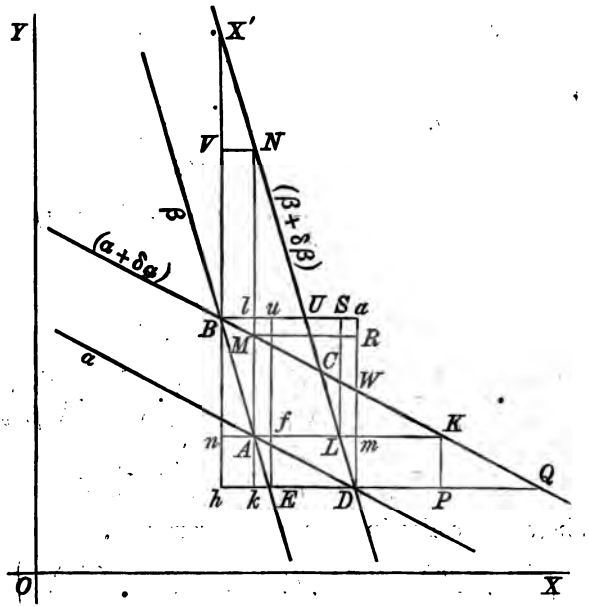
The following is a geometrical proof of (3) for the case in which x, y are the co-ordinates of a point in a plane, and

$$\alpha = f(x, y) = \text{a constant},$$

and

$$\beta = F(x, y) = \text{a constant},$$

are the equations of two lines (straight or curved) in the plane which intersect each other:—



Let OX and OY represent the axes of co-ordinates, and let $ABCD$ be the figure enclosed by the two pairs of consecutive lines,

$$\begin{cases} \alpha = f(x, y) & = \text{a constant}, \\ \alpha + \delta\alpha = f(x + \delta x, y + \delta y) & = \text{a constant}, \end{cases}$$

and

$$\begin{cases} \beta = F(x, y) & = \text{a constant}, \\ \beta + \delta\beta = F(x + \delta x, y + \delta y) & = \text{a constant}. \end{cases}$$

The lines hQ, nK, MR, Ba, VN are parallel to OX, and the lines hX', kN, Eu, LS, Da, PK are parallel to OY.

From Euclid's theorem that parallelograms on the same base and between the same parallels are equal, we get

$$\begin{aligned}
ABCD &= AKQD = AKPk = AK\,.\,Ak,\\
&= ABUL = AlSL = AL\,.\,Al,\\
&= AMWD = AMRm = AM\,.\,Am,\\
&= ABX'N = AnVN = AN\,.\,An,\\
&= ABUL = AlSL = Alam - LSam,\\
&\qquad\qquad\quad = Alam - Aluf,\\
&\qquad\qquad\quad = Alam - Akhn,\\
\text{Therefore,}\quad &\qquad\qquad\quad = Al\,.\,Am - Ak\,.\,An.
\end{aligned}$$

$$AK\,.\,Ak = AL\,.\,Al = AM\,.\,Am = AN\,.\,An = Al\,.\,Am - Ak\,.\,An.$$

Putting for AK, Ak; AL, Al; &c., their values

$$\begin{aligned}
AK &= \left(\frac{dx}{d\alpha}\right)_y \delta\alpha,\\
Ak &= -\left(\frac{dy}{d\beta}\right)_\alpha \delta\beta,\\
AL &= \left(\frac{dx}{d\beta}\right)_y \delta\beta,\\
Al &= \left(\frac{dy}{d\alpha}\right)_\beta \delta\alpha,\\
AM &= \left(\frac{dy}{d\alpha}\right)_x \delta\alpha,\\
Am &= \left(\frac{dx}{d\beta}\right)_\alpha \delta\beta,\\
AN &= \left(\frac{dy}{d\beta}\right)_x \delta\beta,\\
An &= -\left(\frac{dx}{d\alpha}\right)_\beta \delta\alpha;
\end{aligned}$$

and dividing out $\delta\alpha\,.\,\delta\beta$, we obtain the set of equations (3).

CHAPTER II.

ON THE GEOMETRICAL REPRESENTATION OF WORK.

A FORCE is said to do work when it overcomes resistance through space.

For example, when a body is lifted through a height, work is done in overcoming the resistance which we call the weight of the body.

Work is also done in overcoming resistances due to the inertia of matter, friction, elasticity of matter, electricity, and magnetism; as also in overcoming the cohesion of matter, as in planing, sawing, boring, &c.

The work done in overcoming a resistance is measured by the product obtained by multiplying the numerical value of the resistance overcome by the number of units of space through which it is overcome.

The force which overcomes the resistance is called the working force, and the work done by it may also be calculated by multiplying its numerical value by the number of units of space through which its place of application moves along its line of action.

Hence—

Work done by a force in overcoming a resistance

= Resistance × space through which the resistance is overcome.

= Working force × space through which its place of application moves in its direction.

Or if R denote the resistance overcome, s the space through which it is overcome, and W the work done,

$$W = R \,.\, s. \tag{4}$$

Otherwise, if P denote the working force, s the space through which its place of application moves in the direction of its line of action, and W the work done,

$$W = P \,.\, s. \tag{5}$$

If the line of action of the working force, and the line of motion of its place of application, are not coincident, but make an angle θ with each other, then, the letters P and W being used as before, let s denote the distance through which the place of application of the force moves; it follows that $s \,.\, \cos\theta$ will denote the distance through which the place of application of the force moves in the direction of the line of action of the force. Hence

$$W = P \,.\, s \cos\theta.$$

Another mode of procedure in this case is to resolve the force P into two component forces, $P\cos\theta$ and $P\sin\theta$, the former acting in the same direction as P's place of application moves, the latter acting at right angles to the direction of motion.

As the latter component does no work, the work done by the former will be the work done by P.

Hence
$$W = P\cos\theta \times s,$$
$$= Ps\cos\theta, \tag{6}$$

which is the same as was obtained by the other method.

The unit of work will be determined by the units of force and space used.

In the British empire the units of force and space used for practical purposes are the weight of a pound of matter

and a foot of space; and the unit of work is the work done in overcoming a resistance of a pound through a space of a foot. This unit of work is called a *foot-pound.*

For scientific purposes the unit of force employed is the force which, by its action on a pound of matter for a second, would communicate to it a velocity of one foot per second, provided it were originally at rest and that no other force is acting on it.

This unit of force is called a *poundal.*

The scientific unit of work corresponding to this unit of force is the work done in overcoming a resistance of a poundal through a space of a foot.

This unit of work is called a *foot-poundal.*

In France the units of force, space, and work, corresponding to the British pound, foot, and foot-pound, are the gramme, centimetre, and centimetre-gramme.

The French units, dyne, centimetre, and erg, correspond to the British units, poundal, foot, and foot-poundal.

Scientific men of all nations generally use this last system of units, which is called the C.G.S. system—C, denoting centimetre; G, gramme; and S, second.

This system is so called, because the centimetre, gramme, and second are the fundamental units, namely, the units of space, mass, and time.

A straight line is used as the geometrical representation of a force.

The direction of the line represents the direction in which the force acts.

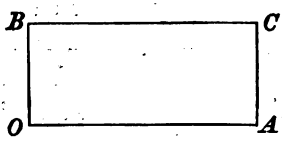
The length of the line represents the magnitude of the force.

Some point in the line (generally one of its extremities) represents the place of application of the force.

In representing the magnitude of a force, a line of unit length is commonly taken to represent a unit of force. But this is not always done: some arbitrary unit of length being often chosen to represent a unit of force.

In geometrical diagrams the unit of space is also often represented by some arbitrary length of line.

To represent geometrically the work done by a force P, whose place of application moves through a space s in the direction of action of the force, construct a rectangle $OACB$, having the side AO s units long, and the side OB P units long.



The area of this rectangle will be $P \cdot s$ square units. Therefore the area of the rectangle is numerically the same as the quantity of work done by the force. Hence the area of the rectangle may be taken as a geometrical representation of the work done by the force.

In drawing such diagrams we may represent the unit of space by any convenient arbitrary length, and the unit of force by the same or any other arbitrary unit of length; then a rectangle having these two arbitrary lengths for adjacent sides will represent a unit of work.

For example, to represent the work done by P lbs. of force acting through s feet of space, and doing W foot-pounds of work, we may represent a foot of space by an inch, and a pound of force by a line a quarter of an inch long. The line OA representing s feet will be s inches, and the line OB representing P lbs. will be P quarters of an inch. Hence the area of $OACB$ will be $\frac{P}{4} \times s = \frac{P \cdot s}{4}$ square inches. But the foot-pound of work is represented by a rectangle having its adjacent sides of lengths one inch and a quarter

of an inch respectively, and having therefore its area a quarter of a square inch. Hence the rectangle $OACB$ will be equal in area to $P.s$ such rectangles, and will therefore represent $P.s$ foot-pounds of work, and will therefore be a geometrical representation of the work done.

Throughout this work, when an area is said to represent a quantity of work, the preceding convention will be implied though not spoken of.

If a varying force act through a space s, the force increasing gradually from P_1 to P_2, or diminishing gradually from P_1 to P_2, there will be an average value of the force intermediate in value between P_1 and P_2, such that the work which would be done by it in acting through the same space s will be equal to the work done by the varying force. Let P denote this average force, then

$$W = P.s.$$

But P is intermediate between P_1 and P_2.

Hence $P.s$ is intermediate between $P_1.s$ and $P_2.s$.

Therefore W is intermediate between $P_1.s$ and $P_2.s$.

If the space s be divided into n parts, each of length $\delta s = \frac{s}{n}$, and if $P_0, P_1, P_2, P_3, \ldots P_n$ denote the values of the force at the beginning of s, at the points of division, and at the end of s; then

Work in first portion of space is intermediate between $P_0 \delta s$ and $P_1 \delta s$.

Work in second portion lies between $P_1.\delta s$ and $P_2.\delta s$.

" third " " $P_2.\delta s$ " $P_3.\delta s$.

. . . . . .

" n^{th} " " $P_{n-1}.\delta s$ " $P_n \delta s$.

Hence if $P_0 < P_1 < P_2 < \ldots . < P_{n-1} < P_n$,

or if $P_0 > P_1 > P_2 > \ldots . > P_{n-1} > P_n$;

that is, if P increase all the time or diminish all the time, the whole work will lie between the sums

$$P_0\delta s + P_1\delta s + P_2\delta s + \ldots + P_{n-1}\delta s,$$

and $$P_1\delta s + P_2\delta s + P_3\delta s + \ldots + P_n\delta s.$$

Now the difference of these two sums is

$$(P_n \sim P_1)\,\delta s = (P_n \sim P_1)\,\frac{s}{n},$$

which diminishes indefinitely as the number of divisions increases.

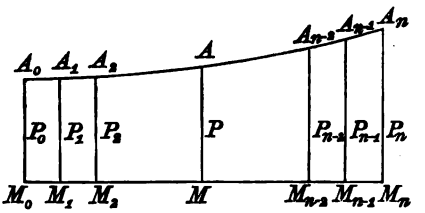
Hence each of these sums will have for its limiting value the work actually performed. Therefore,

$$\begin{aligned} W &= L^t\,\{P_0\delta s + P_1\delta s + \ldots + P_{n-1}\delta s\}, \\ &= L^t\,\Sigma\,(P\,\delta s), \\ &= \int_0^s P\,ds. \end{aligned}$$

Let the straight line $M_0M_1M_2 \ldots M_n$, and the curved line $A_0A_1A_2 \ldots A_n$ be drawn so that

$$M_0M_1 = M_1M_2 = M_2M_3 = \ldots$$

$$= M_{n-1}M_n = \delta s = \frac{s}{n},$$



and the ordinates

$$M_0A_0,\ M_1A_1,\ M_2A_2,\ \ldots\ M_nA_n$$

have the values

$M_0A_0 = P_0$ units of length.
$M_1A_1 = P_1$,, ,,
$M_2A_2 = P_2$,, ,,
. . . . .
$M_nA_n = P_n$,, ,,

and that at every point of the curve the abscissa M_0M and ordinate MA represent simultaneous values of s and P.

Then it may be shown that the area of the figure $A_0 A_1 \ldots A_n M_n \ldots M_0$ is $\text{Area} = \int_0^s P ds.$

Hence this area and the work done are *numerically* equal to each other.

Hence this area is a geometrical representation of the work done by the force.

In this proof it has been assumed that the force either continually increases or continually decreases.

But in other cases the space can be divided into parts for each of which the force continually increases or continually decreases. Hence the proposition holds for each of these, and therefore for the whole space. Therefore the proposition is true generally.

Let p denote the *intensity* of the pressure exerted by an expanding body in overcoming external resistance to its expansion, let δA denote the surface over which the pressure is exerted, and let δv denote the distance through which this resistance is overcome in a very short time δt.

Then the work done by the pressure on the surface δA in time δt will be $p\,\delta A \,.\, \delta v.$

Hence the work done by the pressure over the whole surface in the whole time will be

$$\iint p\, dA\, dv \qquad (7)$$

with the proper limits.

If p is the same at all parts of the surface, as in the case of slowly expanding fluids, or fluids being slowly compressed, the above expression for the work becomes

$$W = \int p\, dv$$

with the proper limits, where

$$dv = \int dv\, dA$$

over the whole surface, v denoting the volume of the fluid.

The important result

$$W = \int p\,dv, \qquad (8)$$

with the proper limits, may be proved more simply for the case of a body expanding in a cylinder and pushing out a piston. For

$$P = Ap,$$

A denoting the area of the piston,
p „ „ intensity of the pressure on the piston.

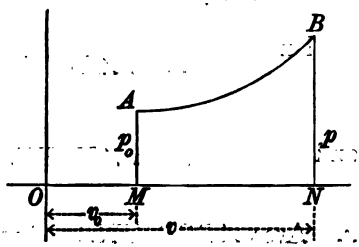
Hence, if s denote the travel of the piston,

$$W = \int_0^s P\,ds,$$

$$= \int_0^s pA\,ds,$$

$$= \int_{v_0}^{v} p\,dv. \qquad (8)$$

Now if a curve be described having v and p for abscissa and ordinate, the area included by the curve, the axis of abscissæ, and the ordinates v_0 and v is



Area $ABNM = \int_{v_0}^{v} p\,dv.$

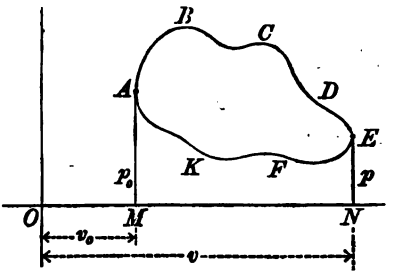
Hence W and this area are numerically equal.

Therefore this area will be a geometrical representation of the work of expansion.

If the fluid is compressed from volume v to volume v_0, the work of compression will be

$$W = \int_{v_0}^{v} p\,dv. \qquad (9)$$

Again, if the fluid go through a cycle of changes, first expanding from volume v_0 to v in a way geometrically represented by $ABCDE$, and suffering compression in a way represented by $EFKA$.



Then the whole external work done by the fluid during the cycle is

$$W = \text{work of expansion} - \text{work of compression},$$

$$= \int_{v_0}^{v} p_H\,dv - \int_{v_0}^{v} p_L\,dv,$$

$$= \int p\,dv, \tag{10}$$

where p_H denotes the value of p on the expansion, and p_L the value of p on the compression.

But
$$\text{Area } ABCDENMA = \int_{v_0}^{v} p_H\,dv,$$

and
$$\text{Area } AKFENMA = \int_{v_0}^{v} p_L\,dv;$$

$$\therefore \quad \text{Area } ABCDEFKA = \text{Area } ABCDENMA - \text{Area } AKFENMA,$$

$$= \int_{v_0}^{v} p_H\,dv - \int_{v_0}^{v} p_L\,dv,$$

$$= \int p\,dv. \tag{11}$$

Hence the area $ABCDEFKA$ is numerically equal to the work W,

$$i.e. \qquad W = \text{Area } ABCDEFKA. \qquad (12)$$

In (10) and (11) the integration is to be carried round the circuit $ABCDEFKA$.

Hence the area of the closed figure $ABCDEFKA$ is a geometrical representation of the work done by the body on external bodies during the cycle of changes.

CHAPTER III.

A SHORT HISTORY OF THERMODYNAMICS.

TILL early in this century the prevailing belief was that heat is a subtle imponderable fluid, filling the pores of bodies as water fills the pores of a sponge. They believed that when heat is added to a body its molecules are forced further apart, causing the body to expand. On the other hand, the abstraction of heat from a body was believed to allow its particles to come closer together, thus permitting the body to contract. They also believed that when a body is rubbed it becomes warmer, because the operation of friction squeezes heat out of it as water exudes from a sponge when it is squeezed.

A few of the earlier philosophers—Bacon, Boyle, and Locke, for example—believed that heat is a kind of molecular motion; their ideas were, however, very vague and barren.

About the end of last century clearer views of the mechanical nature of heat were entertained by Count Rumford and Sir Humphrey Davy.

In 1798 the former, whose name was Benjamin Thompson, was superintending the boring of brass cannon for the Prussian Government at Munich. While thus occupied he was much struck by the very great quantity of the heat developed in the process of boring.

Having made many experiments with borers of different degrees of bluntness, he was led to the conclusion that there is no limit to the greatness of the quantity of heat developable from a pound of brass in reducing it to borings, the quantity of heat so developed increasing proportionately with the bluntness of the borer.

He therefore concluded that the heat developed by friction is not squeezed out of the body rubbed, but is *generated* by the rubbing process. His reason for this conclusion was that a pound of brass, at ordinary temperature, could contain only a *limited* quantity of caloric, and therefore could give out only a *limited* quantity on being rubbed; whereas the quantity *actually* producible by this process from a pound of brass appeared to have *no limit.*

He also observed that the quantity of heat developed appeared to be *proportional to the quantity of work expended in producing it.*

This he verified by specially devised experiments, in which the boring operation was performed under water, with a borer so blunt that little or no borings were produced, heat being the chief product. He even attempted to estimate the numerical relation between the heat produced and the work expended in producing it.

He caused the work to be performed by a pair of horses working at a rate as uniform as possible, and a thermometer placed in the water indicated a nearly uniform rate of rise of temperature.

In one of his experiments a steel borer of known weight was caused to turn inside a brass cylinder of known weight, surrounded by water of known weight contained in a wooden vessel. The capacity of the water and apparatus he estimated to be equal to that of 26·58 lbs. of water.

At the beginning of the experiment the water and apparatus were observed to be at a temperature of 33° F. A horse was kept working uniformly for 2½ hours, when the water was observed to have reached the temperature 212° F., the rate of rise having been observed to be a nearly uniform rate of 1°·3 per minute.

From these data he calculated that the heat required to raise the temperature of a pound of water through 1° F. is equivalent to 847 foot-pounds of work.

This is little more than 10 per cent. greater than the more accurate value, 772, afterwards obtained by Joule. If Rumford had discontinued his experiments at this stage he would very likely have received the full credit of having demonstrated the true nature of heat.

But unfortunately he sought confirmation of his theory in *another* line of argument which has been shown to be fallacious, because it starts from a premiss which is not self-evident, and which had not been proved to be true.

His second line of argument was somewhat as follows:—If the heat developed by the boring process is not *generated* by the process, but is squeezed out of the brass during the process, then a pound of brass borings must contain less heat than a pound of lump brass. Now the calorists held a hypothesis that *the capacity for heat of a body is proportional to the quantity of heat the body has in it.* Hence if a pound of brass borings has less heat in it than a pound of lump brass, the capacity for heat of the former will be less than that of the latter. But experiment showed that they had equal capacities for heat. Therefore they contain equal quantities of heat. Consequently the brass borings lost no heat during the boring process. Therefore the heat developed during the process did not come out of

the brass, but must have been *generated* by the process, and is merely *transmuted work.*

Now as Thomson says—If a clever calorist had agreed to give up the above hypothesis, he would have been "unmoved by Rumford's argument."

In the following year Sir Humphry Davy, independently, proved the immateriality of heat, by showing that when two pieces of ice are rubbed together the ice is changed into water. To prevent communication of heat from surrounding matter, he caused the friction to be performed by clockwork in a vacuum surrounded by pounded ice or snow.

Davy's reasoning, though somewhat confused, is quite convincing. He says:—"From this experiment it is evident that ice by friction is converted into water, and according to the supposition its capacity is diminished; but it is well known that the capacity of water for heat is much greater than that of ice; and ice must have an absolute quantity of heat added to it before it can be converted into water. Friction, consequently, does not diminish the capacity of bodies for heat."

The following I take to be what Davy intended to say:—

Ice must have heat added to it to convert it into water. But ice is converted into water by friction. Therefore friction generates heat.

He seems to have mixed this up with another line of argument, to wit:—

The calorists say that friction developes heat by diminishing the capacity for heat of the body rubbed, and so causing some of its heat to exude. Now friction causes ice to become water: consequently the capacity of water for heat should be less than that of ice. But it is well known that the capacity for heat of water is much greater than that

of ice. Therefore friction does not diminish the capacity for heat of the body rubbed.

This second argument is a fine specimen of *the fallacy of ambiguity of terms.* The term *capacity for heat* is used here in two senses—firstly, in the sense of *Quantity of heat which a body can contain at a given temperature;* secondly, in the sense of the *Quantity of heat which will raise the body's temperature one degree.*

Rumford refrained from speculations as to the nature of the motion constituting heat. He says:—"I am very far from pretending to know how or by what means or mechanical contrivance that particular kind of motion in bodies which has been supposed to constitute heat is excited, continued, and propagated."

Davy, on the other hand, goes on to speculations of which the following are specimens:—"Heat, then, or that power which prevents the actual contact of corpuscles of bodies, and which is the cause of our own sensations of heat and cold, may be defined as a peculiar motion, probably a vibration of the corpuscles of bodies tending to separate them. It may with propriety be called the repulsive motion. Bodies exist in different states, and these states depend on the action of attraction, and of the repulsive power on their corpuscles, or in other words, on their different quantities of repulsion and attraction."

"The immediate cause of the phenomenon of heat, then, is motion; and the laws of its communication are precisely the same as the laws of the communication of motion."

He considers this repulsive motion to be analogous to the orbital motions of planets: and that, consequently, as with planets, so with corpuscles, the greater the velocities the larger the orbits in which they move. Hence, when heat is

added to a solid, its corpuscles move with increased velocities, and, consequently, move round each other in larger orbits, and, as more and more heat is added, the orbits of the corpuscles become larger and larger until they cease to be closed like circles or ellipses or to lie within a finite space, and become unlimited like hyperbolas, analogous to the orbits of comets, whose motions are approximately rectilinear, except when they come into the neighbourhood of attracting bodies, when they suffer deflections, their paths becoming more sensibly curvilinear. In the liquid state the corpuscles are so close together that as soon as a corpuscle gets beyond the sensible influence of a neighbouring corpuscle it comes within the sensible influence of another; hence its path will be a *sinuous* line, made up of little bits of hyperbolas, whose planes and eccentricities will be nearly as numerous as the corpuscles within whose sensible influence it comes. In some cases two or more corpuscles may be so near to each other that their mutual attraction will be so great as to cause them to revolve round their common centre of gravity, and therefore they would form a group moving on in company until they receive some accession of motion either by collision with some other corpuscle or group of corpuscles, or by the addition of more heat to the body. In the *gaseous state* corpuscles have velocities so great that their motions are so little affected by their mutual attractions that, except when they approach very close to each other, their paths are sensibly rectilinear. Hence the path of a corpuscle of a body in the gaseous state will consist of a multitude of straight lines joined together by little bits of hyperbolas. Here also two or more corpuscles may move on together as a group until they come into collision with other corpuscles or groups.

It thus appears that Davy is the founder of the 'Kinetic Theory of Matter.'

These theories of Rumford and Davy received little or no attention from scientific men for about forty years, when they were re-discovered or brought into notice by quite a crowd of scientists working independently of each other. Among the principal of these may be mentioned Mohr, Seguin, Mayer, Colding, and Joule.

Joule determined the dynamical equivalent of heat by a number of finely-conceived and carefully-conducted experiments, the most important of which, for our present purpose, are those *immediately* connecting heat and mechanical energy. These are experiments in which heat is produced by—(1) fluid friction; (2) by the friction of solids; (3) by the compression of gases.

In the first of these he heated water in a churn driven by a heavy weight descending under the influence of gravity. Comparing the work done by gravity on the descending weight with the heat necessary to produce the observed rise of temperature of the water in the churn, he determined the dynamical equivalent of heat to be 772 on the Fahrenheit scale: that is, 772 foot-pounds of work or visible kinetic energy are equivalent to the quantity of heat which will raise the temperature of a pound of water from 32° to 33° F.

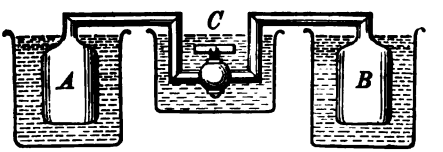
Mayer, in determining the dynamical equivalent of heat, assumed that the heat evolved by air during compression is dynamically equivalent to the work spent in compressing the air.

Joule, after justifying Mayer's assumption by experiment, repeated Mayer's experiment, and found a value of the dynamical equivalent not much different from that obtained by the churning of water.

Joule's experiment, by means of which he justified Mayer's assumption, is as follows:—

Two vessels, of equal capacity—one exhausted, and the other filled with air under a very high pressure (22 atmospheres), and connected by a pipe with a stopcock for opening or closing the communication between the vessels—were placed in a large vessel filled with water rising high enough to cover both vessels. On opening the connexion between the two air-vessels, the temperature of the surrounding water did not experience any change. Joule afterwards repeated the experiment, but, instead of immersing both air-vessels in the same vessel of water, he immersed them in separate vessels of water, and the stopcock in a third vessel of water.

After opening the stopcock, *C*, the water round the air-vessel, *A*, which contained the compressed air, was found to have fallen in temperature, while that of the water round the air-vessel, *B*,* was found to have risen in temperature as much as *A* had fallen. This is accounted for thus:—



The air which rushes from *A* into *B* is expelled from *A* into *B* by the excess of the pressure in *A* over that in *B*. Hence the kinetic energy of the air rushing from *A* into *B* is given to it at the expense of the temperature of the air in *A*, which is expanding against external pressure, and is therefore cooling. The kinetic energy of the air rushing from *A* into *B* is re-converted into heat by impact on the sides of *B*, and by

* The temperature of the water round *B* was found to have risen a very little more than that of the water round *A* had fallen, and the temperature of the water round *C* was found to have risen a very little.

fluid friction. The temperature of the air in *B* therefore rises. The fact of the rise in *B* being equal to the fall in *A* shows that no heat is absorbed or emitted by mere expansion of air.

Joule also found values of this dynamical equivalent of heat from experiments on the friction of mercury and cast iron which differ very little from those obtained by the two preceding methods.

This completes this short history of the First Law of Thermodynamics, which is by Rankine enunciated as follows:—"Heat and mechanical energy are mutually convertible, and heat requires for its production and produces by its disappearance mechanical energy in the proportion of 772 foot-pounds for each British unit of heat."

This statement of the law might be misunderstood, and is often misunderstood, for most people who know only the first law, and have learnt it in this form, suppose that any given quantity of heat may be *wholly* converted into work or mechanical energy, which is very far from being the case, as even in the most favourable circumstances *only a small fraction* of it can be so converted.

This misunderstanding is, of course, corrected when the Second Law is understood; but for the benefit of those who do not go on to the study of the Second Law it will perhaps be as well for them to substitute Thomson's statement of the First Law, which puts it in a form which cannot be misunderstood:—

"*When equal quantities of mechanical effect are produced by any means whatever from purely thermal sources, or lost in purely thermal effects, equal quantities of heat are put out of existence or are generated.*"

It will be convenient to quote here also Thomson's statement of the Second Law, and then give its history, as by

doing so the two laws are brought into juxtaposition, which is advantageous:—

"*If an engine be such that, when it is worked backwards, the physical and mechanical agencies in every part of its motions are all reversed, it produces as much mechanical effect as can be produced by any thermodynamic engine, with the same temperatures of source and refrigerator, from a given quantity of heat.*"

In 1824, Sadi Carnot, in a work entitled 'Reflexions sur la Puissance Motrice du Feu,' &c., first enunciated the *principle of a cycle of operations* in the following terms:—

"*If a body, after having experienced a certain number of transformations, be brought identically to its primitive physical state as to density, temperature, and molecular constitution, it must contain the same quantity of heat as that which it initially possessed;* or, in other words, the quantities of heat lost by the body under one set of operations are precisely compensated by those which are absorbed in the others."

The second part of this enunciation, which I have not italicised, is erroneous, as it assumes heat to be a fluid, and that it passes through a heat-engine *undiminished in quantity* just as water passes through a water-mill undiminished in quantity, and that heat passing from a body of *higher temperature* to one of *lower temperature* is analogous to water passing from a *higher level* to a *lower level*, loss of potential energy being experienced in both cases.

Carnot's further idea of *a reversible cycle* is of extreme importance, and is most accurately enunciated by Thomson in the first portion of his statement of the Second Law of Thermodynamics, which we repeat:—

"*If an engine be such that when it is worked backwards, the physical and mechanical agencies in every part of its motions are all reversed,*" *such an engine is said to be reversible.*

That is, if at any point of the direct cycle the body is receiving heat at a certain rate, and is doing work at a certain rate, it will, at the same point of the reverse cycle, be giving out heat, and having work done upon it at these same rates, and *vice versâ.*

In order that a cycle of transformations may be reversible, the following conditions must hold:—

1. The working body must, at every instant, have the same temperature throughout all its parts.

2. The working body must, at every instant, have the same pressure throughout all its parts.

3. The transformations through which the working body passes must take place so slowly that the densities of all its parts may, at any instant, be the same as they would be if the temperatures and pressures of the parts at that instant were constant.

4. The transformations must take place so slowly that the visible kinetic energy of the working body be so small as to be negligible.

5. The working body must, at every instant, be in contact with external bodies of the same temperature as itself, or with non-conductors.*

The Second Law states *that there is no engine more efficient than a reversible engine*, that is, *there is no more perfect engine than a reversible one.*

Hence a reversible engine is said to be a perfect engine, that is, *reversibility is the criterion of perfection.*

---

* If the working body be complex, that is, if it consist of two or more parts, these parts must separately be subject to the foregoing conditions; and in addition, if in contact, or if separated by conductors, must be, at each instant, of the same temperature. But those parts separated by non-conductors need not be of the same temperature.

Carnot founds his proof of the Second Law on the assumption that *the perpetual motion is impossible.*

Clausius and Thomson substituted for this assumption the following axioms :—

Clausius' axiom :—

> "*It is impossible for a self-acting machine, unaided by any external agency, to convey heat from one body to another at a higher temperature.*"

Thomson's axiom :—

> "*It is impossible, by means of inanimate material agency, to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of surrounding objects.*"

More lately Clausius states his axiom thus :—

> "*Heat cannot of itself* (*i.e. without compensation*) *pass from a colder to a hotter body.*"

Professor Clausius in Germany and Professor W. Thomson (now Sir W. Thomson) in Britain showed that although Carnot's work is to a certain extent affected by Caloristic views, it can easily be modified so as to fit into the Thermodynamic Theory of which it now forms a very large and very important part. Carnot's proof of the Second Law and the modified proofs of Clausius and Thomson will be given in our next chapter.

On these two laws, with the aid of a few definitions and experimental results, is reared the whole of the modern structure of Thermodynamics; Thomson, Clausius, and Joule being the principal builders.

We cannot pass from this chapter without saying that, from a physical theory of his own with regard to the nature

of the molecular motion called heat, Rankine deduced most, if not all, of the results obtained by other physicists.

It is also noteworthy that he was the first to write a systematic treatise on the application of Thermodynamic principles to actual heat-engines.

When Molecular Dynamics comes to be better understood, it is just possible that Rankine may take the foremost place amongst the creators of the science of Thermodynamics.

CHAPTER IV.

THE TWO LAWS OF THERMODYNAMICS.

We have already enunciated these two laws in the last chapter, but shall again enunciate the first law in a more specific form, and then give the proofs of the Second Law due to Carnot, Clausius, and Thomson.

First Law.—If a body undergo a cycle of changes, receiving heat during some portions of the cycle, and giving out heat during other portions, and also doing external work during some portions of the cycle, and having external work expended on it during other portions, the excess of the heat received by the body over the heat given out by it during the cycle is dynamically equivalent to the excess of the external work *done by* the body over the external work *done on* the body during the cycle.

If we make use of the Algebraic Convention of positive and negative quantities, and look upon a quantity of heat *given out* as a *negative quantity taken in*, and also consider a quantity of external work done *on* the body as a *negative* quantity done *by* the body, the above may be stated more shortly thus:—

If a body undergo a cycle of changes during which it receives heat and does external work, the latter is dynamically equivalent to the former.

To state this algebraically, let $H_1, H_2, H_3, \ldots, H_n$

denote the quantities of heat received during the different stages of the cycle, W_1, W_2, W_3, ... , W_n the quantities of external work done during these stages, and J, Joule's dynamical equivalent of heat; then

$$J(H_1 + H_2 + H_3 + \ldots + H_n) = W_1 + W_2 + W_3 + \ldots + W_n,$$

or

$$J \,.\, \Sigma(H) = \Sigma(W). \tag{13}$$

If the stages be taken infinitesimally small, (13) will become

$$\left.\begin{aligned} J \int dH &= \int dW \\ &= W \end{aligned}\right\} \tag{14}$$

where W denotes the whole external work done during the cycle.

Putting for W its value given in (10), equation (14) becomes

$$J \int dH = \int p dv. \tag{15}$$

Equations (13) and (15) are both statements of the specific form of the First Law spoken of in this chapter. Of course the summations and integrations are taken round the whole cycle.

Before giving the proofs of the Second Law we shall describe *Carnot's Cycle of Operations.*

The working body is supposed to be contained in a cylinder with non-conducting sides and piston, and having its lower end closed by a perfectly conducting plate.

Let A and B be two bodies kept always at temperatures S and R, S being greater than R, and let C be a non-conducting stand.

Placing the cylinder on A, the working body in the cylinder will quickly attain the temperature S, because the bottom of the cylinder is a perfect conductor; or if we suppose

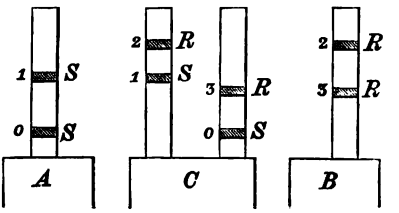
the working body and A to be perfect conductors, the working body will instantaneously acquire the temperature S.

We will suppose that the bodies A and B and the working body are perfect conductors, or that the changes which the working body undergoes take place so slowly that it has at all times the same temperature throughout all its parts.

Starting with the cylinder standing on A, the operations the working body is subjected to are as follows:—

First.—Allow the piston to rise from position 0 to position 1, during which it will do external work, W_1, and receive heat, H_1, from A, and will remain constantly at temperature, S.

Second.—Placing the cylinder on C, let the piston rise from position 1 to position 2, during which it will do external work, W_2, and receive heat, H_2 (= 0), and fall in temperature from S to R.



Third.—Transferring the cylinder from C to B, push the piston down from position 2 to position 3, till the heat, $-H_3$ (using the algebraic convention), given out to B is equal to H_1, the temperature of the working body remaining constantly R during the operation, and work, $-W_3$, being done on the body.

Fourth.—Placing the cylinder again on C, push the piston down from position 3 to position 0, during which work, $-W_4$, is done on the working body, and it emits heat, $-H_4$ (= 0).

The working body having on the whole received no heat, and having reached its original density, will also, by Carnot's axiom, have reached its original temperature, S.

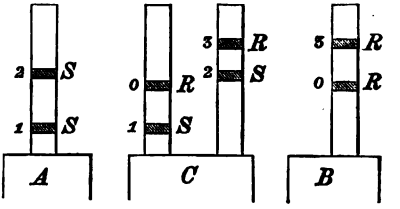
In this cycle, from Carnot's point of view, the heat emitted during the third operation is equal to the heat taken in during the first.

This is inconsistent with the Thermodynamic theory.

To adapt Carnot's cycle to this theory, Professor James Thomson proposed to describe the third operation differently from Carnot. He says:—"We should not say in the third operation, compress till the same amount of heat is given out as was taken in during the first. But we should say, compress till we have let out so much heat that the further compression (during the fourth stage) to the original volume may give back the original temperature."

This correction would be an improvement on the cycle even from Carnot's point of view. For the axiom does not say that if a body experience a series of transformations, at the end of which its density and the quantity of heat it possesses are the same as they were at first, its temperature will be the same as at first, but the converse of this.

Clerk Maxwell proposed to avoid this periphrasis by making the fourth operation the first. Doing so, the cycle will be as follows:—



Placing the cylinder on B, the working body will acquire the temperature R. The operations will then be—

First.—Placing the cylinder on C, push the piston down from position 0 to position 1, so that the temperature of the working body may rise from R to S. The heat, $-H_1$, given out during this operation is zero, because the body is enclosed by non-conductors, and the work done on the body is $-W_1$.

Second.—Transferring the cylinder from C to A, allow the piston to rise through any height from position 1 to position 2, during which let $H_2 = H$ be the heat received by the body, and W_2 the work done by it. The temperature of the body continues to be S during this operation.

Third.—Placing the cylinder on C, allow the piston to rise from position 2 to position 3 until the temperature of the working body falls from S to R.

In this operation the heat H_3 taken in is zero, because the body is enclosed by non-conductors, and the external work done may be denoted by W_3.

Fourth.—Place the cylinder on B, and push down the piston from position 3 to position 0.

In this operation the external work done on the working body may be denoted by $-W_4$, and the heat given out by the body by $-H_4 = h$.

The working body has now returned to its original state of volume and temperature, and therefore of pressure.

The excess of the heat taken in over the heat given out is, by the First Law, dynamically equivalent to the excess of the external work done by the body over the external work done on the body. Hence

$$J\{(H_2 + H_3) - [(-H_1) + (-H_4)]\} = (W_2 + W_3) - [(-W_1) + (-W_4)],$$

or $$J(H_1 + H_2 + H_3 + H_4) = W_1 + W_2 + W_3 + W_4;$$

or since $H_1 = 0 = H_3$, $H_2 = H$, and $H_4 = -h$, this becomes

$$J(H - h) = W_1 + W_2 + W_3 + W_4$$
$$= W, \qquad (16)$$

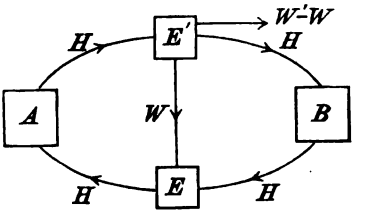
a particular example of (13).

Having thus given some idea as to the nature of a cycle of operations, we shall give the various proofs of the Second Law.

The following is Carnot's proof :—

If possible, let E' be an engine more perfect than the reversible engine E.

Let E' work *forwards*, receiving H units of heat from A, and giving H units to B, and at the same time doing W' units of external work.



Let also E be worked *backwards*, receiving H units of heat from B, and giving out H units to A, and having W units of work done on it.

Now since E' is more perfect than E, W' will be greater than W.

Hence if E' be made to drive E, there will be a balance of external work, $W' - W$, which may be usefully applied.

Hence this system of engines will constitute an automatic engine capable of doing useful work without on the whole any transference of heat; that is, the perpetual motion would be realized. Now this is contrary to all experience. Therefore E' cannot be more perfect than E.

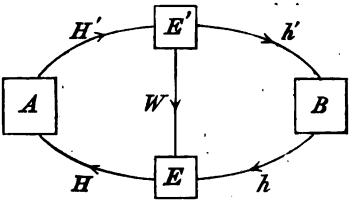
It follows as a corollary to this that *all reversible heat-engines are equally efficient.*

This proof requires modification to make it fit into the Thermodynamic theory. We proceed accordingly to present the modifications given by Clausius and Thomson. Both Clausius and Thomson were obliged to substitute another axiom instead of that of the impossibility of the perpetual motion used by Carnot.

These axioms have been already given in the third chapter.

Clausius' proof is as follows :—

Let, as before, E' be more perfect than the reversible engine E, and let E' be worked forwards, while E is compelled to work backwards.



Let E' receive H' units of heat from A, and give h' units to B, and *do* W units of work.

Let also E receive h units of heat from B, give H units to A, and have W units of work *done on* it.

If now, as before, E and E' be coupled so that E' shall drive E, the system will constitute a complex engine, doing no external work, but transferring per cycle $H - H'$ or $h - h'$ units of heat from B, the colder body, to A, the warmer, unaided by any external agency, which by the axiom is impossible. Hence E' is not more perfect than E.

It may, perhaps, not be quite evident that H is greater than H', and h than h', but it can be proved easily thus :—

From (13), $J(H' - h') = W = J(H - h)$.

Also since E''s efficiency is greater than E's,

$$\frac{H' - h'}{H'} > \frac{H - h}{H}.$$

From these $\quad H' - h' = H - h,$

and $\quad H' < H;$

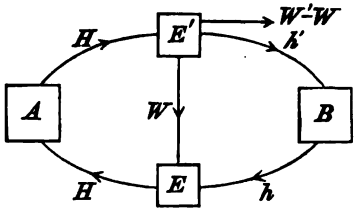
$$\therefore \quad h' < h,$$

and $\quad h - h' = H - H'.$

Thomson, not being quite satisfied with Clausius' Axiom, substituted his own for it, and a corresponding modification of the foregoing proof.

His proof is somewhat as follows:—

Let E', supposed more perfect than E, work *forwards*, receiving H units of heat from A, giving h' units to B, and doing W' units of work.



Let E be worked *backwards*, receiving h units of heat from B, giving H units to A, and having W units of work done *on* it.

Now since E' is more efficient than E,

$$\frac{H-h'}{H} > \frac{H-h}{H};$$

$$\therefore \quad H-h' > H-h, \text{ or } h > h';$$

$$\therefore \quad J(H-h') > J(H-h), \text{ or } W' > W.$$

Hence E' may be caused to drive E, and the whole will form a complex automatic engine, drawing $h-h'$ units of heat from B, and performing $W'-W$ units of external work per cycle.

We may, without interfering with the assumed state of matters, suppose all other surrounding bodies and space to have the same temperature as A. Our complex machine would then continually draw heat from a body B, surrounded by others of a higher temperature, and convert it into work, which is contrary to the assumed axiom. Hence E' is not more efficient than E.

Thus the Second Law is established.

From the Second Law it follows that *all reversible engines are equally perfect.*

Since all reversible heat-engines are equally perfect, their efficiency will be *independent of the physical nature of the working bodies.* Consequently *the efficiency of a perfect heat-engine,*

working between two given temperatures, will depend on these temperatures only, that is, *will be a function of these two temperatures only.*

Now, if these two temperatures differ infinitesimally, the efficiency of the engine will be a function of either of these multiplied by their difference. This function is called *Carnot's Function.* Hence if μ denote Carnot's Function,

$$\text{Efficiency} = \mu \times \text{range of temperature.}$$

Or

$$\text{Carnot's Function} = \frac{\text{Efficiency of engine}}{\text{Range of temperature}}. \qquad (17)$$

Hence if such an engine work with a source and refrigerator at temperatures $t + \delta t$ and t, and if in a cycle it receive $h + \delta h$ units of heat from the source, and give h units to the refrigerator, it will do $J\delta h$ units of external work. The efficiency of this engine will therefore be

$$\text{Efficiency} = \frac{\text{heat converted into work}}{\text{heat received from source}}$$

$$= \frac{\delta h}{h + \delta h}.$$

Therefore

$$\mu = \text{Carnot's Function}$$

$$= \frac{\dfrac{\delta h}{h + \delta h}}{\delta t}$$

$$= \frac{1}{h + \delta h} \cdot \frac{\delta h}{\delta t}.$$

Or, since δt and therefore δh are infinitesimal,

$$\left.\begin{aligned} \mu &= \frac{1}{h} \cdot \frac{dh}{dt} \\ &= \frac{d}{dt}(\log h) \end{aligned}\right\}. \qquad (18)$$

CHAPTER V.

THERMAL LINES AND CYCLIC DIAGRAMS.

A *thermal line*, or *thermogram*, is a line whose co-ordinates represent geometrically the volume and pressure of a body which are varying according to some law.

An *isogram* is a line whose co-ordinates represent the varying volume and pressure of a body undergoing changes of volume and pressure, subject to the law or condition that some property of the body, or some quantity which is a function of its volume and pressure, remains *constant* while these changes are going on.

A *thermograph* is a figure whose perimeter consists of portions of thermal lines or thermograms.

An *isograph* is a quadrilateral of which one pair of opposite sides are isograms of one kind, and the other pair of opposite sides are isograms of another kind.

The principal isograms are *isotherms*, *isobars*, *isomegs*, *isentropes*, *isenergs*, that is, lines of *constant temperature*, *pressure*, *volume*, *entropy*, *energy*.

The principal isographs are those representing the *isothermentropicycle*, the *isobarythermocycle*, the *isothermomegacycle*, the *isobarentropicycle*, the *isentropimegacycle*, the *isobarymegacycle*, the *isenergentropicycle*, the *isobarenergicycle*, the *isenergimegacycle*, and the *isothermenergicycle*.

The meanings of these terms will be understood when it

is observed that therm, bar, meg, energ, are portions of Greek words meaning warm, heavy, large, active.

An *isotherm* is a *constant temperature* thermal line or thermogram.

An *isobar* is a *constant pressure* thermogram. (This is also called an *isopiestic*.)

An *isomeg* is a *constant volume* thermogram (also called an *isometric line*).

An *isentrope* or *adiabatic* is a *constant entropy* thermogram, or it is a line whose co-ordinates have the same relation to each other as the volume and pressure of the body have to each other when they are varied without allowing heat to pass into or out of the body.

An *isenerg* is a *constant energy* isogram (also called an isodynamic line).

An *isothermentropicycle* is a cycle represented by an isograph contained by a pair of *isotherms* and a pair of *isentropes*.

An *isobarythermocycle* is a cycle represented by an isograph contained by a pair of *isobars* and a pair of *isotherms*.

An *isothermomegacycle* is a cycle whose isograph consists of two *isotherms* and two *isomegs*.

An *isobarentropicycle* is a cycle whose isograph consists of two *isobars* and two *isentropes*.

An *isentropimegacycle* is a cycle whose isograph consists of two *isentropes* and two *isomegs*.

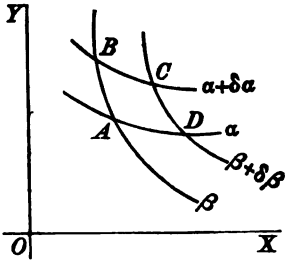
An *isobarymegacycle* is a cycle whose isograph consists of two *isobars* and two *isomegs*.

An *isenergentropicycle* is a cycle whose isograph consists of two *isenergs* and two *isentropes*.

An *isobarenergicycle* is a cycle whose isograph consists of two *isobars* and two *isenergs*.

An *isenergimegacycle* is a cycle whose isograph consists of two *isenergs* and two *isomegs*.

An *isothermenergicycle* is a cycle whose isograph consists of two *isotherms* and two *isenergs*.



The first of these represents Carnot's Cycle.

Let OX and OY represent the axes of volume and pressure.

Let AD and BC be isograms of the same kind, having for their equations

$$\left.\begin{aligned} & f(v,p) = \alpha = \text{a constant}, \\ \text{and} \quad & f(v,p) = \alpha + \delta\alpha = \text{a constant}. \end{aligned}\right\} \qquad (19)$$

And let AB and DC be two isograms of another kind, having for their equations

$$\left.\begin{aligned} & F(v,p) = \beta = \text{a constant}, \\ \text{and} \quad & F(v,p) = \beta + \delta\beta = \text{a constant}. \end{aligned}\right\} \qquad (20)$$

Then the figure $ABCD$ is an isograph, and if $\delta\alpha$ and $\delta\beta$ are very small, $ABCD$ will be approximately a parallelogram.

Returning to Chapter I. we see that the area of the isograph $ABCD$ is expressible by either of the following expressions:—

$$\left.\begin{aligned} \text{Area of } ABCD &= -\left(\frac{dv}{d\alpha}\right)_p \cdot \left(\frac{dp}{d\beta}\right)_\alpha \cdot \delta\alpha \,.\, \delta\beta \\ \text{or} \qquad &= \left(\frac{dv}{d\beta}\right)_p \cdot \left(\frac{dp}{d\alpha}\right)_\beta \cdot \delta\alpha \,.\, \delta\beta \\ \text{or} \qquad &= \left(\frac{dv}{d\beta}\right)_\alpha \cdot \left(\frac{dp}{d\alpha}\right)_v \cdot \delta\alpha \,.\, \delta\beta \end{aligned}\right\} \qquad (21)$$

$$\left.\begin{aligned} \text{or} \quad &= -\left(\frac{dv}{da}\right)_\beta \cdot \left(\frac{dp}{d\beta}\right)_v \cdot \delta a \,.\, \delta\beta \\ \text{or} \quad &= \left\{ \left(\frac{dv}{d\beta}\right)_a \cdot \left(\frac{dp}{da}\right)_\beta - \left(\frac{dv}{da}\right)_\beta \cdot \left(\frac{dp}{d\beta}\right)_a \right\} \delta a \,.\, \delta\beta \end{aligned}\right\} \quad (21)$$

and the work of the cycle will be algebraically expressed by either of these five expressions. That is,

$$\left.\begin{aligned} W &= \text{area of } ABCD \\ &= -\left(\frac{dv}{da}\right)_p \cdot \left(\frac{dp}{d\beta}\right)_a \cdot \delta a \,.\, \delta\beta \\ \text{or} \quad &= \left(\frac{dv}{d\beta}\right)_p \cdot \left(\frac{dp}{da}\right)_\beta \cdot \delta a \,.\, \delta\beta \\ \text{or} \quad &= \left(\frac{dv}{d\beta}\right)_a \cdot \left(\frac{dp}{da}\right)_v \cdot \delta a \,.\, \delta\beta \\ \text{or} \quad &= -\left(\frac{dv}{da}\right)_\beta \cdot \left(\frac{dp}{d\beta}\right)_v \cdot \delta a \,.\, \delta\beta \\ \text{or} \quad &= \left\{ \left(\frac{dv}{d\beta}\right)_a \cdot \left(\frac{dp}{da}\right)_\beta - \left(\frac{dv}{da}\right)_\beta \cdot \left(\frac{dp}{d\beta}\right)_a \right\} \delta a \,.\, \delta\beta \end{aligned}\right\} . \quad (22)$$

Again, if $\left(\frac{dH}{da}\right)_\beta$ and $\left(\frac{dH}{d\beta}\right)_a$ denote the rates at which the working body takes in heat in passing from state A to state B, and from state A to state D, per unit increase of a and β respectively. Then

$$\left(\frac{dH}{da}\right)_{\beta+\delta\beta} \text{ and } \left(\frac{dH}{d\beta}\right)_{a+\delta a}$$

will denote the rates at which it takes in heat in passing from state D to state C, and from state B to state C, per unit increase of a and β respectively.

Therefore the algebraic sum of the quantities of heat taken in during the cycle will be

$\int dH$ = heat taken in from A to B + heat taken in from B to C + heat taken in from C to D + heat taken in from D to A.

$$= \left(\frac{dH}{d\alpha}\right)_\beta \delta\alpha + \left(\frac{dH}{d\beta}\right)_{\alpha+\delta\alpha} \delta\beta - \left(\frac{dH}{d\alpha}\right)_{\beta+\delta\beta} \delta\alpha - \left(\frac{dH}{d\beta}\right)_\alpha \delta\beta$$

$$= \left[\left(\frac{dH}{d\beta}\right)_{\alpha+\delta\alpha} - \left(\frac{dH}{d\beta}\right)_\alpha\right] \delta\beta - \left[\left(\frac{dH}{d\alpha}\right)_{\beta+\delta\beta} - \left(\frac{dH}{d\alpha}\right)_\beta\right] \delta\alpha$$

$$= \left\{\left(\frac{d}{d\alpha}\right)_\beta \left(\frac{dH}{d\beta}\right)_\alpha - \left(\frac{d}{d\beta}\right)_\alpha \left(\frac{dH}{d\alpha}\right)_\beta\right\} \delta\alpha\, \delta\beta. \qquad (23)$$

But byt he First Law (14),

$$J \int dH = W;$$

$\therefore$ substituting from (22) and (23)

$$\left.\begin{aligned} J\left\{\left(\frac{d}{d\alpha}\right)_\beta \left(\frac{dH}{d\beta}\right)_\alpha - \left(\frac{d}{d\beta}\right)_\alpha \left(\frac{dH}{d\alpha}\right)_\beta\right\} &= \left(\frac{dv}{d\beta}\right)_\alpha \cdot \left(\frac{dp}{d\alpha}\right)_\beta \\ &\quad - \left(\frac{dv}{d\alpha}\right)_\beta \cdot \left(\frac{dp}{d\beta}\right)_\alpha \\ &= -\left(\frac{dv}{d\alpha}\right)_p \cdot \left(\frac{dp}{d\beta}\right)_\alpha \\ &= \left(\frac{dv}{d\beta}\right)_p \cdot \left(\frac{dp}{d\alpha}\right)_\beta \\ &= \left(\frac{dv}{d\beta}\right)_\alpha \cdot \left(\frac{dp}{d\alpha}\right)_v \\ &= -\left(\frac{dv}{d\alpha}\right)_\beta \cdot \left(\frac{dp}{d\beta}\right)_v \end{aligned}\right\} \qquad (24)$$

Multiplying both sides of these by

$$\left(\frac{d\alpha}{dt}\right)_\beta \left(\frac{d\beta}{dt}\right),$$

and substituting for

$$\left(\frac{dH}{d\alpha}\right)_\beta \text{ and } \left(\frac{dH}{d\beta}\right)_\alpha$$

their equivalents

$$\left(\frac{dH}{dt}\right)_\beta \cdot \left(\frac{dt}{d\alpha}\right)_\beta = c_\beta \cdot \left(\frac{dt}{d\alpha}\right)_\beta \text{ and } \left(\frac{dH}{dt}\right)_\alpha \cdot \left(\frac{dt}{d\beta}\right)_\alpha = c_\alpha \cdot \left(\frac{dt}{d\beta}\right)_\alpha,$$

we get

$$\left.\begin{aligned} &J\left\{\left(\frac{d\beta}{dt}\right)_\alpha\left(\frac{d}{dt}\right)_\beta\left[c_\alpha\left(\frac{dt}{d\beta}\right)_\alpha\right] - \left(\frac{d\alpha}{dt}\right)_\beta\left(\frac{d}{dt}\right)_\alpha\left[c_\beta\left(\frac{dt}{d\alpha}\right)_\beta\right]\right\} \\ &\qquad = \left(\frac{dv}{dt}\right)_\alpha\left(\frac{dp}{dt}\right)_\beta - \left(\frac{dv}{dt}\right)_\beta\left(\frac{dp}{dt}\right)_\alpha \\ \text{or}\quad &J\left\{c_\alpha\left(\frac{d}{dt}\right)_\beta \log\left[c_\alpha\left(\frac{dt}{d\beta}\right)_\alpha\right] - c_\beta\left(\frac{d}{dt}\right)_\alpha \log\left[c_\beta\left(\frac{dt}{d\alpha}\right)_\beta\right]\right\} \\ &\qquad = \left(\frac{dv}{dt}\right)_\alpha\left(\frac{dp}{dt}\right)_\beta - \left(\frac{dv}{dt}\right)_\beta\left(\frac{dp}{dt}\right)_\alpha \end{aligned}\right\} \quad (24^*)$$

where c_α = specific heat, α constant,
and c_β = ,, ,, β constant.

This expression of the First Law is not so general as that of (14), but is more easily applied to the solution of many problems.

In Carnot's Cycle, or the Isothermentropicycle, $\alpha = t$, $\beta = \phi$, where t and ϕ denote temperature and entropy,

$$\left(\frac{dH}{d\alpha}\right)_\beta = \left(\frac{dH}{dt}\right)_\phi = 0,$$

$$\left(\frac{dH}{d\beta}\right)_\alpha = \left(\frac{dH}{d\phi}\right)_t,$$

$$\frac{dH}{d\alpha}\Big)_{\beta+\delta\beta} = \left(\frac{dH}{dt}\right)_{\phi+\delta\phi} = 0,$$

and

$$\left(\frac{dH}{d\beta}\right)_{\alpha+\delta\alpha} = \left(\frac{dH}{d\phi}\right)_{t+\delta t}.$$

Substituting in (24) we get

$$J\left(\frac{d}{dt}\right)_\phi\left[\left(\frac{dH}{d\phi}\right)_t\right] = \left(\frac{dv}{d\phi}\right)_t\left(\frac{dp}{dt}\right)_v;$$

$$\therefore\quad J\frac{\left(\frac{d}{dt}\right)_\phi\left[\left(\frac{dH}{d\phi}\right)_t\right]}{\left(\frac{dH}{d\phi}\right)_t} = \frac{\left(\frac{dv}{d\phi}\right)_t\left(\frac{dp}{dt}\right)_v}{\left(\frac{dH}{d\phi}\right)_t},$$

or

$$J\left(\frac{d}{dt}\right)_\phi\left[\log\left(\frac{dH}{d\phi}\right)_t\right] = \frac{\left(\frac{dp}{dt}\right)_v}{\left(\frac{dH}{dv}\right)_t}. \tag{25}$$

But if in (18) we put for h its value

$$\left(\frac{dH}{d\phi}\right)_t\delta\phi,$$

we get

$$\mu = \left(\frac{d}{dt}\right)_\phi\left[\log\left(\frac{dH}{d\phi}\right)_t\right]. \tag{26}$$

Substituting this in (25) we get

$$J\mu = \frac{\left(\frac{dp}{dt}\right)_v}{\left(\frac{dH}{dv}\right)_t},$$

or

$$\mu = \frac{\left(\frac{dp}{dt}\right)_v}{J\,.\left(\frac{dH}{dv}\right)_t}. \tag{27}$$

For $\left(\frac{dH}{dv}\right)_t$, which denotes the latent heat of dilatation (*i.e.* the quantity of heat absorbed by the body per unit

increase of volume, the temperature remaining unaltered), Thomson and others use M, while some use l.

$$\therefore \quad \left(\frac{dH}{d\phi}\right)_t = \left(\frac{dH}{dv}\right)_t \left(\frac{dv}{d\phi}\right)_t$$

$$= l\left(\frac{dv}{d\phi}\right)_t \text{ or } M\left(\frac{dv}{d\phi}\right)_t.$$

Hence (25), (26), and (27) become

$$J\left(\frac{d}{dt}\right)_\phi \left\{\log\left[M\left(\frac{dv}{d\phi}\right)_t\right]\right\} = \frac{\left(\frac{dp}{dt}\right)_v}{M}. \tag{28}$$

$$\mu = \left(\frac{d}{dt}\right)_\phi \left\{\log\left[M\left(\frac{dv}{d\phi}\right)_t\right]\right\}. \tag{29}$$

and

$$\mu = \frac{\left(\frac{dp}{dt}\right)_v}{JM}. \tag{30}$$

Equation (28) is an expression of the First Law of Thermodynamics.

Equations (29) and (30) are expressions of the Second Law.

CHAPTER VI.

EXTENSION OF THE SECOND LAW.

INTEGRATING equation (26) we get

$$\log \Phi + \int \mu dt = \log \left(\frac{dH}{d\phi}\right)_t,$$

or

$$\Phi \,.\, e^{\int \mu dt} = \left(\frac{dH}{d\phi}\right)_t, \tag{31}$$

where Φ may be constant or a function of ϕ.

Hence the isentropes may be numbered in any manner consistent with (31).

The simplest way of doing this seems to be as follows:—

Let Φ = a constant = $\frac{1}{J}$ say. Then (31) becomes

$$J\left(\frac{dH}{d\phi}\right)_t = e^{\int \mu dt}, \tag{32}$$

which determines the numbering of the isentropes. For from this we see that the numerical value of ϕ increases by 1 for every quantity of heat equal to $\frac{1}{J} e^{\int \mu dt}$ added while the temperature remains constantly t.

Hence if a quantity of heat, H, be added to a body kept at a constant temperature t, the entropy of the body will increase by

$$\frac{JH}{e^{\int \mu dt}} \text{ or } JHe^{-\int \mu dt},$$

that is,

$$JHe^{-\int \mu dt} = \text{increase of entropy.} \tag{33}$$

Therefore, if quantities of heat $H_1, H_2, H_3, \ldots H_n$ be absorbed by the working body while passing from entropy ϕ_0 to ϕ_1 at temperature t_1, from entropy ϕ_1 to ϕ_2 at temperature t_2, from entropy ϕ_2 to ϕ_3 at temperature t_3, ... , from entropy ϕ_{n-1} to ϕ_n at temperature t_n, (33) gives

$$H_1 e^{-\int \mu_1 dt} + H_2 e^{-\int \mu_2 dt} + H_3 e^{-\int \mu_3 dt} + \ldots + H_n e^{-\int \mu_n dt}$$

$$= \frac{1}{J} \{ (\phi_1 - \phi_0) + (\phi_2 - \phi_1) + (\phi_3 - \phi_2) + \ldots + (\phi_n - \phi_{n-1}) \}$$

$$= \frac{1}{J} (\phi_n - \phi_0);$$

or more shortly,

$$\Sigma (H . e^{-\int \mu dt}) = \frac{1}{J} (\phi_n - \phi_0). \tag{34}$$

Now if the body go through a *cycle* of changes,

$$\phi_n = \phi_0.$$

Hence (34) becomes

$$\Sigma (H . e^{-\int \mu dt}) = 0. \tag{35}$$

If the temperature of the working body change *gradually*, (35) becomes

$$\int e^{-\int \mu dt} . dH = 0. \tag{36}$$

We shall see later that (35) and (36) include the extension of the Second Law found by Thomson and Clausius, namely,

$$\Sigma \left(\frac{q}{t} \right) = 0, \tag{37}$$

and

$$\int \frac{dq}{t} = 0, \tag{38}$$

where q stands for our H, and t denotes the absolute temperature of the working body.

Thomson and Clausius both speak of cycles for which (37) or (38) would *not* be true, but do not make it plain what

is the nature of such cycles. They say that these equations are only satisfied when the cycles are reversible. But they do not make it quite clear what they mean by reversible cycles. Tait, however, says "that any cycle is reversible if the working substance be throughout in contact either with non-conductors or with bodies at its own temperature."

Now the proof here given seems to me to be independent of this assumption for a simple body. All that is assumed are the first four assumptions mentioned in Chapter III.; and that t is *the temperature of the working body*, and dH or dq a small quantity of heat absorbed by this body at temperature t.

We shall now perform the integration indicated in (36) for the elementary cycle figured in Chapter V.

Equation (36) may be written as follows for that cycle:—

$$0 = \int_{\alpha}^{\alpha+\delta\alpha} e^{-\int \mu dt}\left(\frac{dH}{d\alpha}\right)_{\beta} d\alpha + \int_{\beta}^{\beta+\delta\beta} e^{-\int \mu dt}\left(\frac{dH}{d\beta}\right)_{\alpha+\delta\alpha} d\beta$$

$$+ \int_{\alpha+\delta\alpha}^{\alpha} e^{-\int \mu dt}\left(\frac{dH}{d\alpha}\right)_{\beta+\delta\beta} d\alpha + \int_{\beta+\delta\beta}^{\beta} e^{-\int \mu dt}\left(\frac{dH}{d\beta}\right)_{\alpha} d\beta$$

$$= \int_{\beta}^{\beta+\delta\beta} \left\{ \left[e^{-\int \mu dt}\left(\frac{dH}{d\beta}\right)_{\alpha} \right]_{\alpha+\delta\alpha} - \left[e^{-\int \mu dt}\left(\frac{dH}{d\beta}\right)_{\alpha} \right]_{\alpha} \right\} d\beta$$

$$- \int_{\alpha}^{\alpha+\delta\alpha} \left\{ \left[e^{-\int \mu dt}\left(\frac{dH}{d\alpha}\right)_{\beta} \right]_{\beta+\delta\beta} - \left[e^{-\int \mu dt}\left(\frac{dH}{d\alpha}\right)_{\beta} \right]_{\beta} \right\} d\alpha$$

$$= \int_{\beta}^{\beta+\delta\beta} \left\{ \left(\frac{d}{d\alpha}\right)_{\beta} \left[e^{-\int \mu dt}\left(\frac{dH}{d\beta}\right)_{\alpha} \right] \delta\alpha \right\} d\beta$$

$$- \int_{\alpha}^{\alpha+\delta\alpha} \left\{ \left(\frac{d}{d\beta}\right)_{\alpha} \left[e^{-\int \mu dt}\left(\frac{dH}{d\alpha}\right)_{\beta} \right] \delta\beta \right\} d\alpha.$$

Now, since δa and $\delta\beta$ are infinitesimal, the subjects of integration may be supposed constant throughout the integration.

Hence the above becomes

$$0 = \left(\frac{d}{da}\right)_\beta \left[e^{-\int \mu dt}\left(\frac{dH}{d\beta}\right)_a\right] . \delta a . \delta\beta$$

$$- \left(\frac{d}{d\beta}\right)_a \left[e^{-\int \mu dt}\left(\frac{dH}{da}\right)_\beta\right] . \delta\beta . \delta a.$$

Hence, dividing by $\delta a . \delta\beta$, performing the differentiations indicated, and dividing by $e^{-\int \mu dt}$, we get

$$0 = \left(\frac{d}{da}\right)_\beta \left(\frac{dH}{d\beta}\right)_a - \left(\frac{d}{d\beta}\right)_a \left(\frac{dH}{da}\right)_\beta$$

$$- \mu \left\{\left(\frac{dH}{d\beta}\right)_a \left(\frac{dt}{da}\right)_\beta - \left(\frac{dH}{da}\right)_\beta \left(\frac{dt}{d\beta}\right)_a\right\};$$

$$\therefore \quad \mu = \frac{\left(\frac{d}{da}\right)_\beta \left(\frac{dH}{d\beta}\right)_a - \left(\frac{d}{d\beta}\right)_a \left(\frac{dH}{da}\right)_\beta}{\left(\frac{dH}{d\beta}\right)_a \left(\frac{dt}{da}\right)_\beta - \left(\frac{dH}{da}\right)_\beta \left(\frac{dt}{d\beta}\right)_a}. \tag{39}$$

Multiplying numerator and denominator of this by

$$\left(\frac{da}{dt}\right)_\beta . \left(\frac{d\beta}{dt}\right)_a,$$

and putting for $\left(\frac{dH}{da}\right)_\beta$ and $\left(\frac{dH}{d\beta}\right)_a$ their equivalents

$$\left(\frac{dH}{dt}\right)_\beta \left(\frac{dt}{da}\right)_\beta = c_\beta \left(\frac{dt}{da}\right)_\beta \text{ and } \left(\frac{dH}{dt}\right)_a \left(\frac{dt}{d\beta}\right)_a = c_a . \left(\frac{dt}{d\beta}\right)_a,$$

we get

$$\mu = \frac{c_\alpha\left(\frac{d}{dt}\right)_\beta \log\left[c_\alpha\left(\frac{dt}{d\beta}\right)_\alpha\right] - c_\beta\left(\frac{d}{dt}\right)_\alpha \log\left[c_\beta\left(\frac{dt}{d\alpha}\right)_\beta\right]}{c_\alpha - c_\beta}. \quad (39)^*$$

This and (24)* give

$$\mu = \frac{\left(\frac{dv}{dt}\right)_\alpha \cdot \left(\frac{dp}{dt}\right)_\beta - \left(\frac{dv}{dt}\right)_\beta \cdot \left(\frac{dp}{dt}\right)_\alpha}{J\,(c_\alpha - c_\beta)}. \quad (39)^\dagger$$

Equations (24) and (39) are the expressions of the First and Second Laws of Thermodynamics, which will be made use of in the remainder of this book.

CHAPTER VII.

ALGEBRAIC EXPRESSIONS FOR VARIOUS CYCLES.

The Isothermentropicycle, or (t, ϕ) cycle.

Here $\alpha = t$, and $\beta = \phi$;

$$\therefore \quad \left(\frac{dH}{d\alpha}\right)_\beta = \left(\frac{dH}{dt}\right)_\phi = 0,$$

$$\left(\frac{dH}{d\beta}\right)_\alpha = \left(\frac{dH}{d\phi}\right)_t = \left(\frac{dH}{dv}\right)_t \left(\frac{dv}{d\phi}\right)_t = M\left(\frac{dv}{d\phi}\right)_t,$$

where M is the *latent heat of dilatation* of the working body, that is, the quantity of heat it absorbs per unit increase of volume, its temperature being kept constant.

$$\therefore \quad \left(\frac{d}{d\beta}\right)_\alpha \left(\frac{dH}{d\alpha}\right)_\beta = 0,$$

$$\left(\frac{d}{d\alpha}\right)_\beta \left(\frac{dH}{d\beta}\right)_\alpha = \left(\frac{d}{dt}\right)_\phi \left[M\left(\frac{dv}{d\phi}\right)_t\right].$$

Hence (24) becomes

$$\left.\begin{aligned} J\left(\frac{d}{dt}\right)_\phi \left[M\left(\frac{dv}{d\phi}\right)_t\right] &= \left(\frac{dv}{d\phi}\right)_t \cdot \left(\frac{dp}{dt}\right)_\phi - \left(\frac{dv}{dt}\right)_\phi \cdot \left(\frac{dp}{d\phi}\right)_t \\ &= -\left(\frac{dv}{dt}\right)_p \cdot \left(\frac{dp}{d\phi}\right)_t \\ &= \left(\frac{dv}{d\phi}\right)_p \cdot \left(\frac{dp}{dt}\right)_\phi \end{aligned}\right\} \quad (40)$$

$$\left.\begin{aligned} &= \left(\frac{dv}{d\phi}\right)_t \cdot \left(\frac{dp}{dt}\right)_v \\ &= -\left(\frac{dv}{dt}\right)_\phi \left(\frac{dp}{d\phi}\right)_v \end{aligned}\right\} \tag{40}$$

and (39) becomes

$$\left.\begin{aligned} \mu &= \frac{\left(\frac{d}{dt}\right)_\phi \left[M\left(\frac{dv}{d\phi}\right)_t\right]}{M\left(\frac{dv}{d\phi}\right)_t} \\ &= \left(\frac{d}{dt}\right)_\phi \left\{\log\left[M\left(\frac{dv}{d\phi}\right)_t\right]\right\} \end{aligned}\right\} \tag{41}$$

From (40) and (41),

$$\mu = \frac{\left(\frac{dp}{dt}\right)_v}{JM}; \tag{42}$$

and other four expressions, by using the other four values of $\left(\frac{d}{dt}\right)_\phi \left[M\left(\frac{dv}{d\phi}\right)_t\right]$ given in (40).

The Isobarythermocycle, or (p, t) cycle.

In this cycle $\alpha = p$ and $\beta = t$;

$$\therefore \quad \left(\frac{dH}{d\alpha}\right)_\beta = \left(\frac{dH}{dp}\right)_t = \left(\frac{dH}{dv}\right)_t \cdot \left(\frac{dv}{dp}\right)_t$$

$$= M\left(\frac{dv}{dp}\right)_t,$$

$$\left(\frac{dH}{d\beta}\right)_\alpha = \left(\frac{dH}{dt}\right)_p = K = \text{specific heat pressure constant};$$

$$\therefore \quad \left(\frac{d}{d\beta}\right)_\alpha \left(\frac{dH}{d\alpha}\right)_\beta = \left(\frac{d}{dt}\right)_p \left\{M\left(\frac{dv}{dp}\right)_t\right\}$$

and $$\left(\frac{d}{d\alpha}\right)_\beta \left(\frac{dH}{d\beta}\right)_\alpha = \left(\frac{d}{dp}\right)_t [K].$$

Hence (24) becomes

$$\left.\begin{aligned} J\left\{\left(\frac{dK}{dp}\right)_t - \left(\frac{d}{dt}\right)_p\left[M\left(\frac{dv}{dp}\right)_t\right]\right\} &= \left(\frac{dv}{dt}\right)_p \\ &= -\left(\frac{dv}{dp}\right)_t \cdot \left(\frac{dp}{dt}\right)_v \end{aligned}\right\} \quad (43)$$

and (39) becomes

$$\left.\mu = \frac{\left(\frac{dK}{dp}\right)_t - \left(\frac{d}{dt}\right)_p\left[M\left(\frac{dv}{dp}\right)_t\right]}{-M\left(\frac{dv}{dp}\right)_t}\right\} \quad (44)$$

The Isothermomegacycle, or (t, v) cycle.

In this cycle $\alpha = t$, and $\beta = v$;

$$\therefore \quad \left(\frac{dH}{d\alpha}\right)_\beta = \left(\frac{dH}{dt}\right)_v = N = \text{specific heat volume constant,}$$

$$\left(\frac{dH}{d\beta}\right)_\alpha = \left(\frac{dH}{dv}\right)_t = M = \text{latent heat of dilatation;}$$

$$\therefore \quad \left(\frac{d}{d\beta}\right)_\alpha\left(\frac{dH}{d\alpha}\right)_\beta = \left(\frac{dN}{dv}\right)_t,$$

$$\left(\frac{d}{d\alpha}\right)_\beta\left(\frac{dH}{d\beta}\right)_\alpha = \left(\frac{dM}{dt}\right)_v.$$

Substituting in (24) we get

$$J\left\{\left(\frac{dM}{dt}\right)_v - \left(\frac{dN}{dv}\right)_t\right\} = \left(\frac{dp}{dt}\right)_v. \quad (45)$$

Substituting in (39) we get

$$\mu = \frac{\left(\frac{dM}{dt}\right)_v - \left(\frac{dN}{dv}\right)_t}{M}. \quad (46)$$

From (43) and (44), and also from (45) and (46), equation (42) is reproduced.

The Isobarentropicycle, or (p, ϕ) cycle.

Here $\alpha = p$, and $\beta = \phi$;

$$\therefore \quad \left(\frac{dH}{d\alpha}\right)_\beta = \left(\frac{dH}{dp}\right)_\phi = 0,$$

$$\left(\frac{dH}{d\beta}\right)_\alpha = \left(\frac{dH}{d\phi}\right)_p = \left(\frac{dH}{dt}\right)_p \cdot \left(\frac{dt}{d\phi}\right)_p = K\left(\frac{dt}{d\phi}\right)_p,$$

$$\left(\frac{d}{d\beta}\right)_\alpha \left(\frac{dH}{d\alpha}\right)_\beta = 0,$$

$$\left(\frac{d}{d\alpha}\right)_\beta \left(\frac{dH}{d\beta}\right)_\alpha = \left(\frac{d}{dp}\right)_\phi \left[K\left(\frac{dt}{d\phi}\right)_p\right].$$

Substituting in (24) we get

$$J\left(\frac{d}{dp}\right)_\phi \left\{K\left(\frac{dt}{d\phi}\right)_p\right\} = \left(\frac{dv}{d\phi}\right)_p. \tag{47}$$

Substituting in (39) we get

$$\mu = \frac{\left(\frac{d}{dp}\right)_\phi \left\{K\left(\frac{dt}{d\phi}\right)_p\right\}}{K\left(\frac{dt}{d\phi}\right)_p \left(\frac{dt}{dp}\right)_\phi}$$

$$= \left(\frac{d}{dp}\right)_\phi \left\{\log\left[K\left(\frac{dt}{d\phi}\right)_p\right]\right\} \left(\frac{dp}{dt}\right)_\phi$$

$$= \left(\frac{d}{dt}\right)_\phi \left\{\log\left[K\left(\frac{dt}{d\phi}\right)_p\right]\right\}. \tag{48}$$

From (47) and (48),

$$\mu = \frac{\left(\frac{dv}{d\phi}\right)_p}{J.K.\left(\frac{dt}{d\phi}\right)_p \cdot \left(\frac{dt}{dp}\right)_\phi}$$

$$= \frac{1}{J.K} \cdot \left(\frac{dv}{dt}\right)_p \cdot \left(\frac{dp}{dt}\right)_\phi. \tag{49}$$

The Isentropimegacycle, or (ϕ, v) *cycle.*

$$\alpha = \phi, \text{ and } \beta = v;$$

$$\therefore \quad \left(\frac{dH}{d\alpha}\right)_\beta = \left(\frac{dH}{d\phi}\right)_v = \left(\frac{dH}{dt}\right)_v \cdot \left(\frac{dt}{d\phi}\right)_v = N \cdot \left(\frac{dt}{d\phi}\right)_v,$$

$$\left(\frac{dH}{d\beta}\right)_\alpha = \left(\frac{dH}{dv}\right)_\phi = 0,$$

$$\left(\frac{d}{d\beta}\right)_\alpha \left(\frac{dH}{d\alpha}\right)_\beta = \left(\frac{d}{dv}\right)_\phi \left[N\left(\frac{dt}{d\phi}\right)_v\right]$$

$$\left(\frac{d}{d\alpha}\right)_\beta \left(\frac{dH}{d\beta}\right)_\alpha = 0.$$

Substituting in (24) we get

$$-J\left(\frac{d}{dv}\right)_\phi \left\{N\left(\frac{dt}{d\phi}\right)_v\right\} = \left(\frac{dp}{d\phi}\right)_v. \tag{50}$$

From (39) we get

$$u = \frac{-\left(\frac{d}{dv}\right)_\phi \left\{N\left(\frac{dt}{d\phi}\right)_v\right\}}{-N\left(\frac{dt}{d\phi}\right)_v \left(\frac{dt}{dv}\right)_\phi}$$

$$= \left(\frac{d}{dv}\right)_\phi \left\{\log\left[N\left(\frac{dt}{d\phi}\right)_v\right]\right\} \left(\frac{dv}{dt}\right)_\phi;$$

$$= \left(\frac{d}{dt}\right)_\phi \left\{\log\left[N\left(\frac{dt}{d\phi}\right)_v\right]\right\}. \tag{51}$$

From (50) and (51),

$$\mu = \frac{\left(\frac{dp}{d\phi}\right)_v}{-JN\left(\frac{dt}{d\phi}\right)_v \left(\frac{dt}{dv}\right)_\phi}$$

$$= -\frac{1}{JN}\left(\frac{dp}{dt}\right)_v \left(\frac{dv}{dt}\right)_\phi. \tag{52}$$

The Isobarymegacycle, or (p, v) cycle.

$\alpha = p$, and $\beta = v$;

$$\therefore \quad \left(\frac{dH}{d\alpha}\right)_\beta = \left(\frac{dH}{dp}\right)_v = \left(\frac{dH}{dt}\right)_v \cdot \left(\frac{dt}{dp}\right)_v = N \cdot \left(\frac{dt}{dp}\right)_v,$$

$$\left(\frac{dH}{d\beta}\right)_\alpha = \left(\frac{dH}{dv}\right)_p = \left(\frac{dH}{dt}\right)_p \cdot \left(\frac{dt}{dv}\right)_p = K \cdot \left(\frac{dt}{dv}\right)_p,$$

$$\left(\frac{d}{d\beta}\right)_\alpha \left(\frac{dH}{d\alpha}\right)_\beta = \left(\frac{d}{dv}\right)_p \left[N\left(\frac{dt}{dp}\right)_v\right],$$

$$\left(\frac{d}{d\alpha}\right)_\beta \cdot \left(\frac{dH}{d\beta}\right)_\alpha = \left(\frac{d}{dp}\right)_v \left[K\left(\frac{dt}{dv}\right)_p\right].$$

Substituting in (24) we get

$$J\left\{\left(\frac{d}{dp}\right)_v \left[K\left(\frac{dt}{dv}\right)_p\right] - \left(\frac{d}{dv}\right)_p \left[N\left(\frac{dt}{dp}\right)_v\right]\right\} = 1. \qquad (53)$$

From (39) we get

$$\mu = \frac{\left(\frac{d}{dp}\right)_v \left[K\left(\frac{dt}{dv}\right)_p\right] - \left(\frac{d}{dv}\right)_p \left[N\left(\frac{dt}{dp}\right)_v\right]}{\left(K - N\right)\left(\frac{dt}{dv}\right)_p \left(\frac{dt}{dp}\right)_v}. \qquad (54)$$

From (53) and (54) we get

$$\mu = \frac{1}{J\left(K - N\right)\left(\frac{dt}{dv}\right)_p \left(\frac{dt}{dp}\right)_v}$$

$$= \frac{1}{J(K - N)} \cdot \left(\frac{dv}{dt}\right)_p \cdot \left(\frac{dp}{dt}\right)_v. \qquad (55)$$

The Isenergentropicycle, or (E, ϕ) *cycle.*

$\alpha = E,\ \beta = \phi$;

$$\therefore \quad \left(\frac{dH}{d\alpha}\right)_\beta = \left(\frac{dH}{dE}\right)_\phi = 0,$$

$$\left(\frac{dH}{d\beta}\right)_\alpha = \left(\frac{dH}{d\phi}\right)_E.$$

But by definition,

$$\delta E = J\delta H - \delta W,$$
$$= J\delta H - p\delta v;$$

$$\therefore \quad \left(\frac{dH}{dv}\right)_E = \frac{p}{J};$$

$$\therefore \quad \left(\frac{dH}{d\beta}\right)_\alpha = \left(\frac{dH}{d\phi}\right)_E = \left(\frac{dH}{dv}\right)_E \cdot \left(\frac{dv}{d\phi}\right)_E = \frac{p}{J}\left(\frac{dv}{d\phi}\right)_E;$$

$$\therefore \quad \left(\frac{d}{d\beta}\right)_\alpha \left(\frac{dH}{d\alpha}\right)_\beta = 0,$$

and $$\left(\frac{d}{d\alpha}\right)_\beta \left(\frac{dH}{d\beta}\right)_\alpha = \left(\frac{d}{dE}\right)_\phi \left[\frac{p}{J}\left(\frac{dv}{d\phi}\right)_E\right].$$

By substitution in (24) we get

$$\left.\begin{aligned} J\left(\frac{d}{dE}\right)_\phi \left\{\frac{p}{J}\left(\frac{dv}{d\phi}\right)_E\right\} &= \left(\frac{dp}{dE}\right)_\phi \left(\frac{dv}{d\phi}\right)_E - \left(\frac{dp}{d\phi}\right)_E \left(\frac{dv}{dE}\right)_\phi \\ &= -\left(\frac{dp}{d\phi}\right)_E \cdot \left(\frac{dv}{dE}\right)_p \\ &= \left(\frac{dp}{dE}\right)_\phi \cdot \left(\frac{dv}{d\phi}\right)_p \\ &= \left(\frac{dp}{dE}\right)_v \cdot \left(\frac{dv}{d\phi}\right)_E \\ &= -\left(\frac{dp}{d\phi}\right)_v \cdot \left(\frac{dv}{dE}\right)_\phi \end{aligned}\right\} \quad (56)$$

And (39) becomes

$$\mu = \frac{\left(\frac{d}{dE}\right)_\phi \left\{ \frac{p}{J}\left(\frac{dv}{d\phi}\right)_E \right\}}{\frac{p}{J}\left(\frac{dv}{d\phi}\right)_E \cdot \left(\frac{dt}{dE}\right)_\phi}$$

$$= \left(\frac{d}{dE}\right)_\phi \left\{ \log\left[\frac{p}{J}\left(\frac{dv}{d\phi}\right)_E\right] \right\} \left(\frac{dE}{dt}\right)_\phi$$

$$= \left(\frac{d}{dt}\right)_\phi \left\{ \log\left[\frac{p}{J}\left(\frac{dv}{d\phi}\right)_E\right] \right\}. \tag{57}$$

From (56) and (57) we get

$$\mu = \frac{\left(\frac{dp}{dE}\right)_\phi \left(\frac{dv}{d\phi}\right)_E - \left(\frac{dp}{d\phi}\right)_E \cdot \left(\frac{dv}{dE}\right)_\phi}{p\left(\frac{dv}{d\phi}\right)_E \left(\frac{dt}{dE}\right)_\phi}$$

$$= \frac{1}{p}\left\{ \left(\frac{dp}{dt}\right)_\phi - \left(\frac{dp}{dv}\right)_E \left(\frac{dv}{dt}\right)_\phi \right\}. \tag{58}$$

The Isobarenergicycle, or (p, E) cycle.

$\alpha = p$, and $\beta = E$;

$$\therefore \quad \left(\frac{dH}{d\alpha}\right)_\beta = \left(\frac{dH}{dp}\right)_E = \left(\frac{dH}{dv}\right)_E \left(\frac{dv}{dp}\right)_E = \frac{p}{J}\left(\frac{dv}{dp}\right)_E$$

$$\left(\frac{dH}{d\beta}\right)_\alpha = \left(\frac{dH}{dE}\right)_p.$$

But $J\delta H = \delta E + p\delta v$;

$$\therefore \quad J\left(\frac{dH}{dE}\right)_p = 1 + p\left(\frac{dv}{dE}\right)_p;$$

$$\therefore \quad \left(\frac{dH}{d\beta}\right)_\alpha = \frac{1}{J}\left\{1 + p\left(\frac{dv}{dE}\right)_p\right\},$$

or $$\left(\frac{dH}{d\beta}\right)_\alpha = \left(\frac{dH}{dE}\right)_p = \left(\frac{dH}{dt}\right)_p \left(\frac{dt}{dE}\right)_p = K\left(\frac{dt}{dE}\right)_p.$$

Hence by substitution in (24) we get

$$\left.\begin{aligned} & J\left\{\left(\frac{d}{dp}\right)_E\left[K\left(\frac{dt}{dE}\right)_p\right] - \left(\frac{d}{dE}\right)_p\left[\frac{p}{J}\left(\frac{dv}{dp}\right)_E\right]\right\} = \left(\frac{dv}{dE}\right)_p \\ \text{or } & J\left\{\left(\frac{d}{dp}\right)_E\left[\frac{p}{J}\left(\frac{dv}{dE}\right)_p\right] - \left(\frac{d}{dE}\right)_p\left[\frac{p}{J}\left(\frac{dv}{dp}\right)_E\right]\right\} = \left(\frac{dv}{dE}\right)_p \end{aligned}\right\}$$

When the operations here indicated are performed, and the result is simplified, it becomes an identity.

Substituting in (39) we get

$$\mu = \frac{\dfrac{1}{J}\left(\dfrac{dv}{dE}\right)_p}{K\left(\dfrac{dt}{dE}\right)_p \cdot \left(\dfrac{dt}{dp}\right)_E - \dfrac{p}{J}\left(\dfrac{dv}{dp}\right)_E\left(\dfrac{dt}{dE}\right)_p}$$

$$= \frac{\left(\dfrac{dv}{dt}\right)_p}{JK\left(\dfrac{dt}{dp}\right)_E - p\left(\dfrac{dv}{dp}\right)_E}. \qquad (59)$$

The Isenergimegacycle, or (E, v) *cycle.*

$$\alpha = E, \ \beta = v.$$

But $J\delta H = \delta E + p\delta v$;

$$\therefore \quad J\left(\frac{dH}{dE}\right)_v = 1, \text{ and } J\left(\frac{dH}{dv}\right)_E = p;$$

$$\therefore \quad \left(\frac{dH}{d\alpha}\right)_\beta = \left(\frac{dH}{dE}\right)_v = \frac{1}{J},$$

and $$\left(\frac{dH}{d\beta}\right)_\alpha = \left(\frac{dH}{dv}\right)_E = \frac{p}{J};$$

$$\therefore \quad \left(\frac{d}{d\beta}\right)_\alpha \left(\frac{dH}{d\alpha}\right)_\beta = 0,$$

and
$$\left(\frac{d}{d\alpha}\right)_\beta \left(\frac{dH}{d\beta}\right)_\alpha = \left(\frac{d}{dE}\right)_v \left(\frac{p}{J}\right) = \frac{1}{J}\left(\frac{dp}{dE}\right)_v.$$

Hence by substitution (24) becomes

$$\left(\frac{dp}{dE}\right)_v = \left(\frac{dp}{dE}\right)_v;$$

and (39) becomes

$$\left.\begin{aligned} \mu &= \frac{\frac{1}{J}\left(\frac{dp}{dE}\right)_v}{\frac{p}{J}\left(\frac{dt}{dE}\right)_v - \frac{1}{J}\left(\frac{dt}{dv}\right)_E} \\ &= \frac{\left(\frac{dp}{dE}\right)_v}{p\left(\frac{dt}{dE}\right)_v - \left(\frac{dt}{dv}\right)_E} \\ &= \frac{\left(\frac{dp}{dt}\right)_v}{p + \left(\frac{dE}{dv}\right)_t} \end{aligned}\right\} \qquad (60)$$

The Isothermenergicycle, or (t, E) cycle.

$\alpha = t$, and $\beta = E$;

$$\therefore \quad \left(\frac{dH}{d\alpha}\right)_\beta = \left(\frac{dH}{dt}\right)_E = c_E, \text{ and } \left(\frac{dH}{d\beta}\right)_\alpha = \left(\frac{dH}{dE}\right)_t = l_E.$$

But $J\delta H = \delta E + p\delta v$;

$$\therefore \quad J\left(\frac{dH}{dt}\right)_E = p\left(\frac{dv}{dt}\right)_E,$$

and
$$J\left(\frac{dH}{dE}\right)_t = 1 + p\left(\frac{dv}{dE}\right)_t.$$

Hence $$\left(\frac{dH}{d\alpha}\right)_\beta = \left(\frac{dH}{dt}\right)_E = \frac{p}{J}\left(\frac{dv}{dt}\right)_E,$$

and $$\left(\frac{dH}{d\beta}\right)_\alpha = \left(\frac{dH}{dE}\right)_t = \frac{1}{J} + \frac{p}{J}\left(\frac{dv}{dE}\right)_t.$$

Substituting in (24) we get

$$J\left\{\left(\frac{d}{dt}\right)_E\left[\frac{p}{J}\left(\frac{dv}{dE}\right)_t\right]-\left(\frac{d}{dE}\right)_t\left[\frac{p}{J}\left(\frac{dv}{dt}\right)_E\right]\right\}=\left(\frac{dv}{dE}\right)_t\left(\frac{dp}{dt}\right)_E-\left(\frac{dv}{dt}\right)_E\left(\frac{dp}{dE}\right)_t$$

which is an identity.

Substituting in (39) we get

$$\left.\begin{aligned} \mu &= \frac{\left(\frac{dv}{dE}\right)_t\left(\frac{dp}{dt}\right)_E - \left(\frac{dv}{dt}\right)_E \cdot \left(\frac{dp}{dE}\right)_t}{1 + p\left(\frac{dv}{dE}\right)_t} \\ \text{or} \qquad \mu &= \frac{\left(\frac{dl_E}{dt}\right)_E - \left(\frac{dc_E}{dE}\right)_t}{l_E} \end{aligned}\right\} \qquad (61)$$

The (t, β) *cycle.*

$\alpha = t,\ \beta = \beta;$

$$\therefore \quad \left(\frac{dH}{d\alpha}\right)_\beta = \left(\frac{dH}{dt}\right)_\beta = c_\beta = \text{specific heat } \beta \text{ constant,}$$

and $$\left(\frac{dH}{d\beta}\right)_\alpha = \left(\frac{dH}{d\beta}\right)_t = l_\beta = \text{latent heat per unit increase of } \beta.$$

Hence (24) becomes

$$\left.\begin{aligned} J\left\{\left(\frac{dl_\beta}{dt}\right)_\beta - \left(\frac{dc_\beta}{d\beta}\right)_t\right\} &= \left(\frac{dv}{d\beta}\right)_t\left(\frac{dp}{dt}\right)_\beta - \left(\frac{dv}{dt}\right)_\beta\left(\frac{dp}{d\beta}\right)_t \\ &= -\left(\frac{dv}{dt}\right)_p\left(\frac{dp}{d\beta}\right)^t \\ &= \left(\frac{dv}{d\beta}\right)_p\left(\frac{dp}{dt}\right)_\beta \end{aligned}\right\} \qquad (62)$$

$$\left.\begin{aligned} &= \left(\frac{dv}{d\beta}\right)_t \left(\frac{dp}{dt}\right)_v \\ &= -\left(\frac{dv}{dt}\right)_\beta \left(\frac{dp}{d\beta}\right)_v \end{aligned}\right\} \tag{62}$$

and (39) becomes

$$\mu = \frac{\left(\frac{dl_\beta}{dt}\right)_\beta - \left(\frac{dc_\beta}{d\beta}\right)_t}{l_\beta}. \tag{63}$$

This includes (41), (44), (46), and (61); and (62) includes (40), (43), (45).

If in (63) we put $\beta = \phi$, then $c_\beta = c_\phi = 0$;

$$\therefore \quad \mu = \frac{\left(\frac{dl_\phi}{dt}\right)_\phi}{l_\phi}$$

$$= \left(\frac{d}{dt}\right)_\phi \left[\log l_\phi\right];$$

which, since $l_\phi = \left(\frac{dH}{d\phi}\right)_t = e^{\int \mu dt}$, is an identity.

The (α, ϕ) *cycle.*

Here $\alpha = \alpha$, and $\beta = \phi$. Hence $c_\beta = c_\phi = 0$.

Therefore (24)* becomes

$$J \,.\, c^\alpha \,.\left(\frac{d}{dt}\right)_\phi \log\left[c_\alpha\left(\frac{dt}{d\phi}\right)_\alpha\right] = \left(\frac{dv}{dt}\right)_\alpha \left(\frac{dp}{dt}\right)_\phi - \left(\frac{dv}{dt}\right)_\phi \left(\frac{dp}{dt}\right)_\alpha \tag{64}$$

(39)* becomes

$$\mu = \left(\frac{d}{dt}\right)_\phi \log\left[c_\alpha\left(\frac{dt}{d\phi}\right)_\alpha\right]; \tag{65}$$

and (39)† becomes

$$\mu = \frac{\left(\frac{dv}{dt}\right)_\alpha \cdot \left(\frac{dp}{dt}\right)_\phi - \left(\frac{dv}{dt}\right)_\phi \cdot \left(\frac{dp}{dt}\right)_\alpha}{J \,.\, c_\alpha}. \tag{66}$$

Equation (65) includes (48), (51), (57); and (66) includes (49), (52), (58).

CHAPTER VIII.

VALUES OF PARTIAL DIFFERENTIAL COEFFICIENTS.

From (42),

$$\left(\frac{dp}{dt}\right)_v = JM\mu. \tag{67}$$

From (55) and (67),

$$\left(\frac{dv}{dt}\right)_p = \frac{K-N}{M}. \tag{68}$$

From (52) and (67)

$$\left(\frac{dv}{dt}\right)_\phi = -\frac{N}{M}. \tag{69}$$

From (1), (67), and (68),

$$\left(\frac{dv}{dp}\right)_t = -\frac{\left(\frac{dt}{dp}\right)_v}{\left(\frac{dt}{dv}\right)_p} = -\frac{K-N}{JM^2\mu}. \tag{70}$$

From (49) and (68),

$$\left(\frac{dp}{dt}\right)_\phi = \frac{JKM\mu}{K-N}. \tag{71}$$

From (69) and (71),

$$\left(\frac{dp}{dv}\right)_\phi = \left(\frac{dp}{dt}\right)_\phi \cdot \left(\frac{dt}{dv}\right)_\phi$$

$$= -\frac{JKM^2\mu}{N(K-N)}. \tag{72}$$

From (58), (69), and (71),

$$\left(\frac{dp}{dv}\right)_E = \left(\frac{dt}{dv}\right)_\phi \left\{\left(\frac{dp}{dt}\right)_\phi - \mu p\right\}$$

$$= -\frac{M}{N}\left\{\frac{JKM\mu}{K-N} - \mu p\right\}$$

$$= \frac{M\mu}{N}\left\{p - \frac{JKM}{K-N}\right\}. \tag{73}$$

From (60) and (67),

$$\left(\frac{dE}{dv}\right)_t = \frac{1}{\mu}\left(\frac{dp}{dt}\right)_v - p$$

$$= JM - p. \tag{74}$$

From (1) and (74),

$$\left(\frac{dv}{dt}\right)_E = -\left(\frac{dE}{dt}\right)_v \left(\frac{dv}{dE}\right)_t$$

$$= -J\left(\frac{dH}{dt}\right)_v \left(\frac{dv}{dE}\right)_t; \quad \because\ J\delta H = \delta E + p\delta v;$$

$$\therefore\ \left(\frac{dv}{dt}\right)_E = \frac{JN}{p - JM}. \tag{75}$$

From (73) and (75),

$$\left(\frac{dp}{dt}\right)_E = \left(\frac{dp}{dv}\right)_E \cdot \left(\frac{dv}{dt}\right)_E$$

$$= \frac{\mu M}{N}\left\{p - \frac{JKM}{K-N}\right\} \cdot \frac{JN}{p - JM}$$

$$= \frac{JM\mu}{K-N}\left\{K + \frac{pN}{JM - p}\right\}. \tag{76}$$

From (32),

$$JM\left(\frac{dv}{d\phi}\right)_t = J\left(\frac{dH}{dv}\right)_t\left(\frac{dv}{d\phi}\right)_t$$

$$= J\left(\frac{dH}{d\phi}\right)_t$$

$$= e^{\int \mu dt};$$

$$\therefore \quad \left(\frac{dv}{d\phi}\right)_t = \frac{e^{\int \mu dt}}{JM}. \tag{77}$$

From (42), (49), (1), and (77),

$$K\left(\frac{dt}{d\phi}\right)_p = \frac{1}{J\mu}\left(\frac{dv}{dt}\right)_p\left(\frac{dp}{dt}\right)_\phi\left(\frac{dt}{d\phi}\right)_p$$

$$= M\left(\frac{dt}{dp}\right)_v\left(\frac{dv}{dt}\right)_p\left(\frac{dp}{dt}\right)_\phi\left(\frac{dt}{d\phi}\right)_p$$

$$= M\frac{\left(\frac{dt}{dp}\right)_v}{\left(\frac{dt}{dv}\right)_p}\cdot\frac{\left(\frac{dt}{d\phi}\right)_p}{\left(\frac{dt}{dp}\right)_\phi}$$

$$= M\left(\frac{dv}{dp}\right)_t\left(\frac{dp}{d\phi}\right)_t$$

$$= M\left(\frac{dv}{d\phi}\right)_t;$$

$$\therefore \quad \left(\frac{dt}{d\phi}\right)_p = \frac{M}{K}\left(\frac{dv}{d\phi}\right)_t$$

$$= \frac{M}{K}\cdot\frac{e^{\int \mu dt}}{JM} \text{ from (77)}$$

$$= \frac{e^{\int \mu dt}}{JK}. \tag{78}$$

From (69), (1), and (77),

$$JN\left(\frac{dt}{d\phi}\right)_v = -JM\left(\frac{dv}{dt}\right)_\phi \Big/ \left(\frac{dt}{d\phi}\right)_v$$

$$= -JM\frac{\left(\frac{dt}{d\phi}\right)_v}{\left(\frac{dt}{dv}\right)_\phi}$$

$$= JM\left(\frac{dv}{d\phi}\right)_t$$

$$= e^{\int \mu dt};$$

$$\therefore \quad \left(\frac{dt}{d\phi}\right)_v = \frac{e^{\int \mu dt}}{JN}. \tag{79}$$

From (57), (56), (40), (41), and (77),

$$\frac{p}{J}\left(\frac{dv}{d\phi}\right)_E = \frac{1}{\mu}\left(\frac{d}{dt}\right)_\phi\left[\frac{p}{J}\left(\frac{dv}{d\phi}\right)_E\right]$$

$$= \frac{1}{\mu}\left(\frac{d}{dE}\right)_\phi\left[\frac{p}{J}\left(\frac{dv}{d\phi}\right)_E\right]\left(\frac{dE}{dt}\right)_\phi$$

$$= -\frac{1}{J\mu}\cdot\left(\frac{dp}{d\phi}\right)_v\left(\frac{dv}{dE}\right)_\phi\left(\frac{dE}{dt}\right)_\phi$$

$$= -\frac{1}{J\mu}\cdot\left(\frac{dp}{d\phi}\right)_v\left(\frac{dv}{dt}\right)_\phi$$

$$= \frac{1}{\mu}\left(\frac{d}{dt}\right)_\phi\left[M\left(\frac{dv}{d\phi}\right)_t\right]$$

$$= M\left(\frac{dv}{d\phi}\right)_t$$

$$= \frac{1}{J}e^{\int \mu dt};$$

$$\therefore \quad \left(\frac{dv}{d\phi}\right)_E = \frac{1}{p}e^{\int \mu dt}. \tag{80}$$

From (68) and (78),

$$\left(\frac{dv}{d\phi}\right)_p = \left(\frac{dv}{dt}\right)_p \cdot \left(\frac{dt}{d\phi}\right)_p$$

$$= \frac{K-N}{M} \cdot \frac{e^{\int \mu dt}}{JK}$$

$$= \frac{K-N}{JMK} e^{\int \mu dt}. \tag{81}$$

From (67) and (79),

$$\left(\frac{dp}{d\phi}\right)_v = \left(\frac{dp}{dt}\right)_v \cdot \left(\frac{dt}{d\phi}\right)_v$$

$$= JM\mu \cdot \frac{e^{\int \mu dt}}{JN}$$

$$= \frac{M\mu}{N} e^{\int \mu dt}. \tag{82}$$

From (75) and (80),

$$\left(\frac{dt}{d\phi}\right)_E = \left(\frac{dt}{dv}\right)_E \cdot \left(\frac{dv}{d\phi}\right)_E$$

$$= \frac{p - JM}{JN} \cdot \frac{1}{p} e^{\int \mu dt}$$

$$= \frac{p - JM}{JpN} e^{\int \mu dt}. \tag{83}$$

From (70) and (77),

$$\left(\frac{dp}{d\phi}\right)_t = \left(\frac{dp}{dv}\right)_t \cdot \left(\frac{dv}{d\phi}\right)_t$$

$$= -\frac{JM^2\mu}{K-N} \cdot \frac{e^{\int \mu dt}}{JM}$$

$$= -\frac{M\mu}{K-N} e^{\int \mu dt}. \tag{84}$$

From (73) and (80),

$$\left(\frac{dp}{d\phi}\right)_E = \left(\frac{dp}{dv}\right)_E \cdot \left(\frac{dv}{d\phi}\right)_E$$

$$= \frac{M\mu}{N}\left\{p - \frac{JKM}{K-N}\right\}\frac{1}{p}\, e^{\int \mu dt}$$

$$= \frac{M\mu}{pN}\left\{p - \frac{JKM}{K-N}\right\} e^{\int \mu dt}. \tag{85}$$

From (70) and (74),

$$\left(\frac{dp}{dE}\right)_t = \left(\frac{dp}{dv}\right)_t \left(\frac{dv}{dE}\right)_t$$

$$= -\frac{JM^2\mu}{K-N} \cdot \frac{1}{JM-p}$$

$$= \frac{JM^2\mu}{(K-N)(p-JM)}. \tag{86}$$

From (77) and (74),

$$\left(\frac{d\phi}{dE}\right)_t = \left(\frac{d\phi}{dv}\right)_t \cdot \left(\frac{dv}{dE}\right)_t$$

$$= JMe^{-\int \mu dt} \cdot \frac{1}{JM-p}$$

$$= \frac{JM}{JM-p} \cdot e^{-\int \mu dt}. \tag{87}$$

From (1), (74), and (75),

$$\frac{\left(\frac{dt}{dE}\right)_v}{\left(\frac{dt}{dv}\right)_E} = -\left(\frac{dv}{dE}\right)_t;$$

$$\therefore \quad \left(\frac{dt}{dE}\right)_v = -\left(\frac{dv}{dE}\right)_t \cdot \left(\frac{dt}{dv}\right)_E$$

$$= \frac{1}{p - JM} \cdot \frac{p - JM}{JN}$$

$$= \frac{1}{JN}. \tag{88}$$

From (67) and (88),

$$\left(\frac{dp}{dE}\right)_v = \left(\frac{dp}{dt}\right)_v \left(\frac{dt}{dE}\right)_v$$

$$= JM\mu \cdot \frac{1}{JN}$$

$$= \frac{M\mu}{N}. \tag{89}$$

From (79) and (88),

$$\left(\frac{d\phi}{dE}\right)_v = \left(\frac{d\phi}{dt}\right)_v \cdot \left(\frac{dt}{dE}\right)_v$$

$$= JNe^{-\int \mu dt} \cdot \frac{1}{JN}$$

$$= e^{-\int \mu dt}. \tag{90}$$

From (1), (89), and (73),

$$\frac{\left(\frac{dv}{dE}\right)_p}{\left(\frac{dv}{dp}\right)_E} = -\left(\frac{dp}{dE}\right)_v;$$

$$\therefore \quad \left(\frac{dv}{dE}\right)_p = -\left(\frac{dp}{dE}\right)_v \cdot \left(\frac{dv}{dp}\right)_E$$

$$= -\frac{M\mu}{N} \cdot \frac{N}{M\mu} \cdot \frac{K - N}{p(K - N) - JKM}$$

$$= \frac{K - N}{JKM - p(K - N)}. \tag{91}$$

From (68) and (91),

$$\left(\frac{dt}{dE}\right)_p = \left(\frac{dt}{dv}\right)_p \cdot \left(\frac{dv}{dE}\right)_p$$

$$= \frac{M}{K-N} \cdot \frac{K-N}{JKM-p(K-N)}$$

$$= \frac{M}{JKM-p(K-N)}. \tag{92}$$

From (81) and (91),

$$\left(\frac{d\phi}{dE}\right)_p = \left(\frac{d\phi}{dv}\right)_p \cdot \left(\frac{dv}{dE}\right)_p$$

$$= \frac{JMK}{K-N} e^{-\int \mu dt} \cdot \frac{K-N}{JKM-p(K-N)}$$

$$= \frac{JMK}{JKM-p(K-N)} e^{-\int \mu dt}. \tag{93}$$

From (1), (90), and (80),

$$\frac{\left(\frac{dv}{dE}\right)_\phi}{\left(\frac{dv}{d\phi}\right)_E} = -\left(\frac{d\phi}{dE}\right)_v;$$

$$\therefore \quad \left(\frac{dv}{dE}\right)_\phi = -\left(\frac{d\phi}{dE}\right)_v \cdot \left(\frac{dv}{d\phi}\right)_E$$

$$= -e^{-\int \mu dt} \cdot \frac{1}{p} e^{\int \mu dt}$$

$$= -\frac{1}{p}. \tag{94}$$

From (72) and (94),

$$\left(\frac{dp}{dE}\right)_\phi = \left(\frac{dp}{dv}\right)_\phi \cdot \left(\frac{dv}{dE}\right)_\phi$$

$$= \left[-\frac{JKM^2\mu}{N(K-N)}\right] \cdot \left[-\frac{1}{p}\right]$$

$$= \frac{JKM^2\mu}{pN(K-N)}. \qquad (95)$$

From (69) and (94),

$$\left(\frac{dt}{dE}\right)_\phi = \left(\frac{dt}{dv}\right)_\phi \left(\frac{dv}{dE}\right)_\phi$$

$$= \left[-\frac{M}{N}\right] \cdot \left[-\frac{1}{p}\right]$$

$$= \frac{M}{pN}. \qquad (96)$$

We now give a Table of the Partial Differential Coefficients for reference.

TABLE OF PARTIAL DIFFERENTIAL COEFFICIENTS.

Constant.	E.	ϕ.	t.	p.	v.
$\frac{dv}{dp}$	$\frac{-N(K-N)}{\mu M\{JKM-p(K-N)\}}$	$\frac{-N(K-N)}{JKM^2\mu}$	$-\frac{K-N}{JM^2\mu}$	∞	0
$\frac{dv}{dt}$	$\frac{-JN}{JM-p}$	$-\frac{N}{M}$	∞	$\frac{K-N}{M}$	0
$\frac{dv}{d\phi}$	$\frac{e^{\int\mu dt}}{p}$	∞	$\frac{e^{\int\mu dt}}{JM}$	$\frac{K-N}{JMK}e^{\int\mu dt}$	0
$\frac{dv}{dE}$	∞	$-\frac{1}{p}$	$\frac{1}{JM-p}$	$\frac{K-N}{JMK-p(K-N)}$	0
$\frac{dp}{dt}$	$\frac{JM\mu\{JKM-p(K-N)\}}{(K-N)(JM-p)}$	$\frac{JKM\mu}{K-N}$	∞	0	$JM\mu$

$\frac{dp}{d\phi}$	$\frac{M\mu e^{\int \mu dt}\{p(K-N)-JKM\}}{pN(K-N)}$	∞	$\frac{-M\mu e^{\int \mu dt}}{K-N}$	0	$\frac{M\mu}{N} e^{\int \mu dt}$
$\frac{dp}{dE}$	∞	$\frac{JKM^2\mu}{pN(K-N)}$	$\frac{-JM^2\mu}{(K-N)(JM-p)}$	0	$\frac{M\mu}{N}$
$\frac{dt}{d\phi}$	$\frac{-(JM-p)e^{\int \mu dt}}{JpN}$	∞	0	$\frac{e^{\int \mu dt}}{JK}$	$\frac{e^{\int \mu dt}}{JN}$
$\frac{dt}{dE}$	∞	$\frac{M}{pN}$	0	$\frac{M}{JKM-p(K-N)}$	$\frac{1}{JN}$
$\frac{d\phi}{dE}$	∞	0	$\frac{JMe^{-\int \mu dt}}{JM-p}$	$\frac{JMKe^{-\int \mu dt}}{JKM-p(K-N)}$	$e^{-\int \mu dt}$

CHAPTER IX.

COEFFICIENTS OF ELASTICITY AND DILATATION.

THERE are two *Coefficients* or *Moduli* of Elasticity, namely, the *constant temperature modulus* and the *constant entropy modulus*.

The constant temperature modulus of elasticity of volume is measured by the increase of pressure per unit of volume-strain, while the temperature of the body is kept constant.

To put this into algebraic form—

Let δp denote an increase of pressure, and let $-\delta v$ denote the diminution of volume produced by it, while the temperature is kept constantly t.

Then $\dfrac{-\delta v}{v}$ = volume strain.

Then if k_t or k denote the constant temperature modulus of elasticity,

$$k \text{ or } k_t = \frac{\text{stress}}{\text{strain}}$$

$$= \left(\frac{\delta p}{\dfrac{-\delta v}{v}}\right)_t$$

$$= -v\left(\frac{dp}{dv}\right)_t. \qquad (97)$$

The constant entropy modulus of elasticity of volume is measured by the increase of pressure per unit of volume-strain, while the entropy of the body is kept constant (*i.e.* while no heat is taken in or given out by the body).

If k_ϕ denote this modulus, then as before,

$$k_\phi = -v\left(\frac{dp}{dv}\right)_\phi. \tag{98}$$

The coefficient of cubical expansion of a body is the fraction by which its volume-strain increases per unit increase of temperature, while its pressure is kept constant.

To put this into algebraic form, let e denote this coefficient. Then

$$e = \left(\frac{\text{volume-strain}}{\text{increase of temp.}}\right)_p$$

$$= \left(\frac{\frac{\delta v}{v}}{\delta t}\right)_p$$

$$= \frac{1}{v}\left(\frac{dv}{dt}\right)_p. \tag{99}$$

From (97), (99), and (1),

$$k \,.\, e = -v\left(\frac{dp}{dv}\right)_t . \frac{1}{v}\left(\frac{dv}{dt}\right)_p$$

$$= -\frac{\left(\frac{dv}{dt}\right)_p}{\left(\frac{dv}{dp}\right)_t}$$

$$= \left(\frac{dp}{dt}\right)_v. \tag{100}$$

From (42) and (100),

$$\left.\begin{aligned} JM\mu &= ke \\ \text{or} \qquad Jl_v\mu &= k_t \,.\, e \end{aligned}\right\} \tag{101}$$

From (97) and (98),

$$\frac{k_\phi}{k_t} = \frac{-v\left(\dfrac{dp}{dv}\right)_\phi}{-v\left(\dfrac{dp}{dv}\right)_t}$$

$$= \frac{\left(\dfrac{dp}{dv}\right)_\phi}{\left(\dfrac{dp}{dv}\right)_t}$$

$$= \left(\frac{dp}{dv}\right)_\phi \cdot \left(\frac{dv}{dp}\right)_t.$$

But

$$\frac{K}{N} = \frac{\left(\dfrac{dv}{dt}\right)_p \cdot \left(\dfrac{dp}{dt}\right)_\phi}{-\left(\dfrac{dp}{dt}\right)_v \left(\dfrac{dv}{dt}\right)_\phi} \text{ from (49) and (52)}$$

$$= -\frac{\left(\dfrac{dt}{dp}\right)_v}{\left(\dfrac{dt}{dv}\right)_p} \left(\frac{dp}{dv}\right)_\phi$$

$$= \left(\frac{dv}{dp}\right)_t \cdot \left(\frac{dp}{dv}\right)_\phi;$$

$$\left.\begin{aligned} \therefore \quad \frac{k_\phi}{k_t} &= \frac{K}{N} = \gamma \\ &= \frac{c_p}{c_v} = \gamma \end{aligned}\right\} \tag{102}$$

From (55), (99), and (100),

$$J(K - N) = \frac{1}{\mu}\left(\frac{dv}{dt}\right)_p\left(\frac{dp}{dt}\right)_v$$

$$= \frac{1}{\mu} \cdot ev \cdot ke$$

$$= \frac{ke^2v}{\mu}. \tag{103}$$

From (52) and (100),

$$\left(\frac{dt}{dv}\right)_\phi = -\frac{1}{JN\mu}\left(\frac{dp}{dt}\right)_v$$

$$= -\frac{ke}{JN\mu}. \tag{104}$$

But from (103),

$$JN\mu = JK\mu - ke^2v;$$

$\therefore$ (104) becomes

$$\left(\frac{dt}{dv}\right)_\phi = -\frac{ke}{JK\mu - ke^2v}. \tag{105}$$

From (49) and (99),

$$\left(\frac{dt}{dp}\right)_\phi = \frac{1}{JK\mu}\left(\frac{dv}{dt}\right)_p$$

$$= \frac{ev}{JK\mu}. \tag{106}$$

But from (103),

$$JK\mu = JN\mu + ke^2v;$$

$\therefore$ (106) becomes

$$\left(\frac{dt}{dp}\right)_\phi = \frac{ev}{JN\mu + ke^2v}. \tag{107}$$

Some interesting deductions may be drawn from these results.

For example, for such a substance as water between 0° C. and 4° C., which contracts as its temperature is increased, e is negative, and therefore from (104)

$$\left(\frac{dt}{dv}\right)_\phi = \text{a positive quantity.}$$

Hence the temperature of the substance *falls* when it is suddenly compressed.

Again, it may be shown as follows that the temperature of maximum density of water is lowered by increase of pressure :—

$$\left(\frac{dt}{dp}\right)_e = -\frac{\left(\frac{de}{dp}\right)_t}{\left(\frac{de}{dt}\right)_p} \text{ by (1)}$$

$$= -\frac{\left(\frac{d}{dp}\right)_t\left[\frac{1}{v}\left(\frac{dv}{dt}\right)_p\right]}{\left(\frac{de}{dt}\right)_p} \text{ by (99)}$$

$$= \frac{-\left(\frac{d}{dp}\right)_t\left(\frac{d}{dt}\right)_p[\log v]}{\left(\frac{de}{dt}\right)_p}$$

$$= \frac{-\left(\frac{d}{dt}\right)_p\left(\frac{d}{dp}\right)_t(\log v)}{\left(\frac{de}{dt}\right)_p}$$

$$= \frac{-\left(\frac{d}{dt}\right)_p\left[\frac{1}{v}\left(\frac{dv}{dp}\right)_t\right]}{\left(\frac{de}{dt}\right)_p}$$

$$= \frac{\left(\frac{d}{dt}\right)_p \left(\frac{1}{k}\right)}{\left(\frac{de}{dt}\right)_p} \text{ by (97).} \tag{108}$$

But at low temperatures

$$v_{p_0} = 1 + \frac{(t-4)^2}{144000}, \tag{109}$$

where p_0 denotes atmospheric pressure (Thermodynamics, Encycl. Brit.);

$$\therefore \quad \left(\frac{dv}{dt}\right)_{p_0} = \frac{t-4}{72000}. \tag{110}$$

Hence by (99),

$$e = \frac{1}{v}\left(\frac{dv}{dt}\right)_{p_0}$$

$$\doteqdot \frac{t-4}{72000} \text{ by (109) and (110);} \tag{111}$$

$$\therefore \quad \left(\frac{de}{dt}\right)_{p_0} \doteqdot \frac{1}{72000}. \tag{112}$$

Now from Canton's experiments,

$$\left(\frac{d\left(\frac{1}{k}\right)}{dt}\right)_{p_0} = -\cdot 0000003. \tag{113}$$

Hence (108) becomes, by (112) and (113),

$$\left(\frac{dt}{dp}\right)_e \doteqdot \frac{-\cdot 0000003}{\frac{1}{72000}}$$

$$= -\cdot 0216, \tag{114}$$

taking an atmosphere as unit of pressure.

But the expansibility e is zero at the temperature of maximum density;

$$\therefore \quad \left(\frac{dt}{dp}\right)_{\text{max. density.}} = \left(\frac{dt}{dp}\right)_{e=0}$$

$$= - \cdot 0216. \qquad (115)$$

Hence $- 0^{\circ}\cdot 0216$ C. is the change of the temperature of maximum density of water per atmosphere of increase of pressure.

CHAPTER X.

ABSOLUTE SCALE OF TEMPERATURES.

An Absolute Scale of Temperatures is one which is independent of the properties of any particular substance.

Two such scales have been proposed by Thomson, both founded on Carnot's principle.

In his first proposed scale he defines equal differences of temperature as those of the source and refrigerator of a reversible heat-engine, when the quantities of heat transformed into work are equal fractions of the heat taken in.

This scale has not been much used, as it differs to an inconvenient extent from the scales in common use.

The second Absolute Scale proposed by Thomson, which has received universal acceptance from scientific men, and which is of immense theoretical importance, is defined by him thus:—

"*The temperatures of two bodies are proportional to the quantities of heat respectively taken in and given out in localities at one temperature and at the other, respectively, by a material system subjected to a complete cycle of perfectly reversible thermodynamic operations, and not allowed to part with or take in heat at any other temperature:* or *the absolute values of two temperatures are to one another in the proportion of the heat taken in to the heat rejected in a perfect thermodynamic engine, working with a source and refrigerator at the higher and lower of the temperatures respectively.*"

This may be put into algebraic language thus:—

Let τ_1 and τ_2 denote the temperatures of the source and refrigerator of a reversible heat-engine, and let H_1 and H_2 be the quantities of heat received by the engine from the source, and given by it to the refrigerator, respectively, in a cycle of operations.

Then this definition is equivalent to

$$\frac{\tau_1}{\tau_2} = \frac{H_1}{H_2}. \tag{116}$$

If we put for τ_1, τ_2, H_1 and H_2 the expressions $\tau + \delta\tau$, τ, $H + \delta H$, and H (116) becomes

$$\frac{\tau + \delta\tau}{\tau} = \frac{H + \delta H}{H};$$

$$\therefore \quad \frac{\delta\tau}{\tau} = \frac{\delta H}{H}. \tag{117}$$

But from (18),

$$\mu = \frac{1}{H} \cdot \frac{\delta H}{\delta\tau}; \tag{118}$$

$$\left.\begin{aligned} \therefore \quad \mu &= \frac{1}{\tau} \\ \text{or} \quad \tau &= \frac{1}{\mu} \end{aligned}\right\} \tag{119}$$

Hence Absolute temperature is sometimes defined as the reciprocal of Carnot's Function.

This definition must, however, be received with great caution. For, though it is true that the numerical expression for Carnot's Function, derived from the Absolute Scale, is the reciprocal of the corresponding absolute temperature, and *vice versâ*, it does not follow that the numerical value of Carnot's Function, derived from a thermometric scale depending on the properties of some particular substance, is

equal to the reciprocal of the corresponding temperature on the Absolute Scale.

To prove this, let $[\mu]$ denote the numerical value of Carnot's Function derived from the Absolute Scale, and let μ denote its numerical value derived from some other scale, and let τ and t denote the corresponding temperature on these two scales respectively.

Then
$$\mu = \frac{1}{H}\left(\frac{dH}{dt}\right)_\phi \text{ from (18)}$$
$$= \frac{1}{H}\left(\frac{dH}{d\tau}\right)_\phi\left(\frac{d\tau}{dt}\right)_\phi$$
$$= [\mu]\left(\frac{d\tau}{dt}\right)_\phi$$
$$= \frac{1}{\tau}\left(\frac{d\tau}{dt}\right)_\phi, \qquad (120)$$

where H denotes the heat taken in at temperature $\tau + \delta\tau$.

Hence μ will not be equal to $\frac{1}{\tau}$, unless $\frac{d\tau}{dt} = 1$, which is not the case.

To compare the absolute scale with the scale of the constant-pressure air thermometer, let t in (120) denote temperature on the latter scale.

Integrating (120) we get
$$\tau = \tau_0 e^{\int_{t_0}^{t} \mu dt}, \qquad (121)$$

where τ_0 and t_0 denote the freezing temperature on these two scales, and τ and t any other temperature.

To make the two scales agree as well as possible, let
$$\tau_{100} = \tau_0 + 100$$
denote the boiling temperature on the absolute scale.

Then (121) gives

$$\tau_0 + 100 = \tau_0 e^{\int_{t_0}^{t_0+100} \mu dt};$$

$$\therefore \quad \tau_0 = \frac{100}{e^{\int_{t_0}^{t_0+100} \mu dt} - 1}. \qquad (122)$$

Hence if accurate Tables of the value of μ, and therefrom of $e^{\int_{t_0}^{t+100} \mu dt}$ were constructed, the values of τ corresponding to all values of t could be calculated from (121) after finding τ_0 from (122).

Thomson constructed a Table of this sort, but unfortunately, from lack of sufficient data, he assumed that dry steam obeys the thermoelastic laws of gases, and therefore his Tables are somewhat inaccurate.

Using these Tables which are given in his Paper on "Carnot's Theory of the Motive Power of Heat," and observing that his value of μ is equal to the value here used multiplied by $J = 1390$ (Joule's dynamical equivalent).

From Table II.,

$$\int_{t_0}^{t_0+100} \mu dt = \frac{435 \cdot 695}{1390}.$$

Hence (122) becomes

$$\tau_0 = \frac{100}{e^{\frac{435 \cdot 695}{1390}} - 1}$$

$$= \frac{100}{1 \cdot 368 - 1}$$

$$\doteqdot 272.$$

Therefore (121) becomes

$$\tau = 272\, e^{\int_{t_0}^{t} \mu dt}.$$

Hence

$$\tau_{50} = 272\, e^{\int_{t_0}^{t_0+50} \mu dt}$$

$$= 272.e^{\frac{232.185}{1390}} \text{ from Table II.}$$

$$= 272 \times 1{\cdot}182$$

$$= 321^\circ{\cdot}5$$

Also

$$\tau_{150} = 272\, e^{\int_{t_0}^{t_0+150} \mu dt}$$

$$= 272\, e^{\frac{618.142}{1390}} \text{ from Table II.}$$

$$= 272 \times 1{\cdot}56$$

$$= 424^\circ{\cdot}3.$$

From these we get

$$\tau_{50} = 272^\circ + 49^\circ{\cdot}5$$

$$= \tau_0 + 49^\circ{\cdot}5,$$

and

$$\tau_{150} = 272^\circ + 152^\circ{\cdot}3$$

$$= \tau_0 + 152^\circ{\cdot}3.$$

These results, though roughly approximate, are not sufficiently accurate; but we shall indicate another mode of approaching the subject which will give better results.

A scale of absolute temperatures might be constructed immediately without the help of any scale depending on the properties of some thermometric body.

To show this let, in equation (42),

$$t = \tau; \text{ and } \therefore \mu = \frac{1}{\tau},$$

then

$$\frac{1}{\tau} = \frac{1}{JM}\left(\frac{dp}{d\tau}\right)_v;$$

$$\therefore \frac{1}{\tau}\left(\frac{d\tau}{dp}\right)_v = \frac{1}{JM}.$$

Integrating this we get

$$\log \frac{\tau}{\tau_0} = \frac{1}{J} \int_{p_0}^{p} \frac{dp}{M},$$

or

$$\tau = \tau_0 e^{\frac{1}{J}\int_{p_0}^{p} \frac{dp}{M}}, \tag{123}$$

where e is the base of the Naperian logarithms.

To make this agree as nearly as possible with the scales in ordinary use, let

$$\tau_{100} = \tau_0 + 100.$$

Hence (123) gives

$$\tau_0 + 100 = \tau_0 e^{\frac{1}{J}\int_{p_0}^{p_{100}} \frac{dp}{M}};$$

$$\therefore \quad \tau_0 = \frac{100}{e^{\frac{1}{J}\int_{p_0}^{p_{100}} \frac{dp}{M}} - 1}. \tag{124}$$

Now it is evident that the value of M for any temperature, although it depends on that temperature, is independent of any *scale* of temperatures.

Hence, if values of M could be found experimentally for a series of pressures sufficiently close together, the absolute scale might be constructed from it by means of (123) and (124).

In the Article on Heat in the *Encyclopædia Britannica*, Sir W. Thomson shows how this may be done by using a working body consisting of a substance part in one state and part in another state, such as part solid and part liquid, or part liquid and part vapour, or part solid and part vapour; and also indicates how it may be put into practice experimentally in the case of water and steam.

This formula is

$$\tau = \tau_0 e^{\int_{p_0}^{p} \frac{(1-\sigma)\,dp}{J\rho\lambda}}, \tag{125}$$

where σ denotes the ratio of the density of the rarer portion

of the body to that of the denser portion, ρ the density of the rarer portion, and λ the latent heat of transition from the lower to the higher state per unit mass of the substance.

It will be shown later that for such a body

$$M = \frac{\rho\lambda}{1-\sigma}. \tag{126}$$

Hence Thomson's formula is a particular case of (124).

In evaluating

$$\int_{p_0}^{p_{100}} \frac{dp}{M} \text{ and } \int_{p_0}^{p} \frac{dp}{M},$$

the *volume* of the thermometric body *must be kept constant.*

This is not mentioned by Thomson, but in all his experiments the thermometric body consists of two portions of the same substance in different states; in which case τ is a function of p only.

Hence

$$\left(\frac{d\tau}{dp}\right)_v = \left(\frac{d\tau}{dp}\right)_\phi = \left(\frac{d\tau}{dp}\right);$$

and therefore it is unnecessary in this case to attend to the condition of keeping the volume constant during integration.

CHAPTER XI.

RELATION OF THE ABSOLUTE SCALE TO THE SCALE OF THE CONSTANT PRESSURE AIR THERMOMETER.

REGNAULT's experiments have proved that, for air, K, the specific heat under constant pressure, is constant.

Hence
$$\left(\frac{dK}{dp}\right)_t = 0.$$

Therefore (43) becomes

$$-J\left(\frac{d}{dt}\right)_p\left[M\left(\frac{dv}{dp}\right)_t\right] = \left(\frac{dv}{dt}\right)_p$$

or
$$\left(\frac{d}{dt}\right)_p\left\{v + JM\left(\frac{dv}{dp}\right)_t\right\} = 0. \qquad (127)$$

But from (42),

$$JM = \frac{1}{\mu}\left(\frac{dp}{dt}\right)_v;$$

$$\therefore \quad JM\left(\frac{dv}{dp}\right)_t = \frac{1}{\mu}\left(\frac{dp}{dt}\right)_v \cdot \left(\frac{dv}{dp}\right)_t$$

$$= \frac{1}{\mu}\frac{\left(\frac{dp}{dt}\right)_v}{\left(\frac{dp}{dv}\right)_t}$$

$$= -\frac{1}{\mu}\left(\frac{dv}{dt}\right)_p \text{ by (1).} \qquad (128)$$

Hence (127) becomes

$$\left(\frac{d}{dt}\right)_p \left\{ v - \frac{1}{\mu}\left(\frac{dv}{dt}\right)_p \right\} = 0. \tag{129}$$

By integration this becomes

$$v - \frac{1}{\mu}\left(\frac{dv}{dt}\right)_p = P_1, \tag{130}$$

where P_1 is a function of p only, or a constant.

But (120),

$$\mu = \frac{1}{\tau}\left(\frac{d\tau}{dt}\right)_\phi.$$

Now since τ is a function of t only,

$$\left(\frac{d\tau}{dt}\right)_\phi = \left(\frac{d\tau}{dt}\right)_p; \tag{131}$$

$$\therefore \quad \mu = \frac{1}{\tau}\left(\frac{d\tau}{dt}\right)_p. \tag{132}$$

Substituting this in (130) we get

$$v - \tau\left(\frac{dt}{d\tau}\right)_p \cdot \left(\frac{dv}{dt}\right)_p = P_1,$$

or

$$v - \tau\left(\frac{dv}{d\tau}\right)_p = P_1; \tag{133}$$

$$\therefore \quad \frac{\left(\frac{dv}{d\tau}\right)_p}{v - P_1} = \frac{1}{\tau}. \tag{134}$$

Integrating this we get

$$\log (v - P_1) = \log \tau + \log P_2,$$

or

$$v - P_1 = P_2 \tau, \tag{135}$$

where P_2 is a function of p only, or a constant.

But in the constant pressure air-thermometer, where $p = \varpi$ = standard atmospheric pressure,

$$\left.\begin{aligned} t - t_0 &= 100\,\frac{v - v_0}{v_{100} - v_0}; \\ \therefore\quad v &= v_0 + \frac{v_{100} - v_0}{100}\,(t - t_0). \end{aligned}\right\} \tag{136}$$

But from (135) we get

$$\tau = \frac{v - \overline{P_1}}{\overline{P_2}}, \tag{137}$$

where $\overline{P_1}$ and $\overline{P_2}$ are the values of P_1 and P_2 when $p = \varpi$;

$$\therefore\quad \tau_0 = \frac{v_0 - \overline{P_1}}{\overline{P_2}},$$

and

$$\tau_{100} = \frac{v_{100} - \overline{P_1}}{\overline{P_2}};$$

$$\therefore\quad \tau_{100} - \tau_0 = \frac{v_{100} - v_0}{\overline{P_2}},$$

also

$$\tau - \tau_0 = \frac{v - v_0}{\overline{P_2}};$$

$$\therefore\quad \frac{\tau - \tau_0}{\tau_{100} - \tau_0} = \frac{v - v_0}{v_{100} - v_0};$$

$$\therefore\quad \tau - \tau_0 = (\tau_{100} - \tau_0)\,\frac{v - v_0}{v_{100} - v_0}$$

$$= 100\,\frac{v - v_0}{v_{100} - v_0}. \tag{138}$$

Hence from (136) and (138),

$$\left.\begin{aligned} \tau - \tau_0 &= t - t_0, \\ \text{or}\quad \tau - t &= \tau_0 - t_0, \\ &= \gamma \text{ a constant or zero}; \\ \therefore\quad \tau &= t + \gamma. \end{aligned}\right\} \tag{139}$$

Hence temperature on the absolute scale differs from that on the scale of the constant pressure air thermometer by a quantity which has a constant or zero value for all temperatures.

Let us try if the value of γ can be determined by means of the Joule-Thomson experiments on the flow of gases through porous plugs.

The nature of these experiments is concisely described by Tait as follows:—

"The gas to be experimented on is made to pass as uniformly and noiselessly as possible through a tube in which there is an obstruction in the form of a porous plug, such as a pellet of cotton wool or the like. The temperature of the stream is carefully measured on each side of the plug, and at such distances from the plug as to avoid the local irregularities produced by it.

"Since the motion is uniform, equal masses of the gas pass in equal times through the various cross sections of the tube. Let the pressure before and after passing the plug be p and p', the corresponding volumes of unit mass v and v'.

"Then pv is the work done on unit mass of the gas as it passes a cross-section of the tube before reaching the plug, while $p'v'$ is the work it gives out as it passes a section after leaving the plug. Their difference is the gain of energy, provided no heat be supplied from without, and no energy is lost in sound. Hence, since the motion is regarded as uniform, if E and E' be the intrinsic energy of unit mass before and after passing the plug,

$$E' - E = pv - p'v',$$

or the conditions of the experiment are such that $E + pv$ is constant" (Tait's *Heat*).

Let then

$$E + pv = \psi \text{ a constant} \qquad (140)$$

be the equation of the isogram, and let

$$pv = Rt. \tag{141}$$

Then
$$\begin{aligned}
\delta\psi &= \delta(E + pv) \\
&= \delta E + p\delta v + v\delta p \\
&= J\delta H + v\delta p \text{ by definition of } E \\
&= J\left\{\left(\frac{dH}{dt}\right)_p \delta t + \left(\frac{dH}{dp}\right)_t \delta p\right\} + v\delta p \\
&= J\left(\frac{dH}{dt}\right)_p \delta t + \left[J\left(\frac{dH}{dp}\right)_t + v\right]\delta p \\
&= JK\,.\,\delta t + \left[J\left(\frac{dH}{dv}\right)_t\left(\frac{dv}{dp}\right)_t + v\right]\delta p \\
&= JK\delta t + \left[JM\left(\frac{dv}{dp}\right)_t + v\right]\delta p \\
&= JK\delta t + \left[\frac{1}{\mu}\left(\frac{dp}{dt}\right)_v\left(\frac{dv}{dp}\right)_t + v\right]\delta p \text{ by (42)} \\
&= JK\delta t + \left[v - \frac{1}{\mu}\left(\frac{dv}{dt}\right)_p\right]\delta p \text{ by (1)} \\
&= JK\delta t + \left[v - \tau\frac{R}{p}\right]\delta p \text{ from (141)} \\
&= JK\delta t + \left[v - (t+\gamma)\frac{v}{t}\right]\delta p \text{ by (139) and (141)} \\
&= JK\delta t - \frac{v\gamma}{t}\,\delta p \\
&= JK\delta t - \frac{R\gamma}{p}\,\delta p \text{ by (141).}
\end{aligned} \tag{142}$$

Integrating between limits, we get

$$\psi_2 - \psi_1 = JK(t_2 - t_1) - R\gamma \log\frac{p_2}{p_1}. \tag{143}$$

But since ψ is constant

$$\psi_2 = \psi_1.$$

Hence (143) becomes

$$0 = JK(t_2 - t_1) - R\gamma \log\left(\frac{p_2}{p_1}\right);$$

$$\therefore \quad \gamma = \frac{JK(t_2 - t_1)}{R \log\left(\frac{p_2}{p_1}\right)}. \tag{144}$$

But, unfortunately, the Joule-Thomson experiments show that

$$\frac{JK(t_2 - t_1)}{R \log\left(\frac{p_2}{p_1}\right)}$$

is not constant.

Hence it must follow that (141) is not strictly true for gases.

The Joule-Thomson experiments give

$$\left(\frac{dt}{dp}\right) = A\left(\frac{\tau_0}{\tau}\right)^2, \tag{145}$$

where A is a constant.

Now in proving (142) we got

$$\delta\psi = JK\delta t + \left[v - \frac{1}{\mu}\left(\frac{dv}{dt}\right)_p\right]\delta p. \tag{146}$$

Hence
$$\left(\frac{dt}{dp}\right)_\psi = \frac{\frac{1}{\mu}\left(\frac{dv}{dt}\right)_p - v}{JK}$$

$$= \frac{\tau\left(\frac{dt}{d\tau}\right)_p\left(\frac{dv}{dt}\right)_p - v}{JK} \text{ by (132)}$$

$$= \frac{\tau\left(\frac{dv}{d\tau}\right)_p - v}{JK}. \tag{147}$$

From (145) and (147) we have

$$\frac{\tau\left(\frac{dv}{d\tau}\right)_p - v}{JK} = A\left(\frac{\tau_0}{\tau}\right)^2;$$

$$\therefore \quad \tau\left(\frac{dv}{d\tau}\right)_p - v = JKA\left(\frac{\tau_0}{\tau}\right)^2. \tag{148}$$

Hence

$$\left.\begin{aligned} \left(\frac{d\psi}{dp}\right)_\tau &= v - \tau\left(\frac{dv}{d\tau}\right)_p \\ &= -JKA\left(\frac{\tau_0}{\tau}\right)^2. \\ \text{But} \quad \left(\frac{d\psi}{d\tau}\right)_p &= JK. \end{aligned}\right\} \tag{149}$$

Now

$$\left.\begin{aligned} &\left(\frac{d}{dp}\right)_\tau\left(\frac{d\psi}{d\tau}\right)_p = \left(\frac{d}{d\tau}\right)_p\left(\frac{d\psi}{dp}\right)_\tau; \\ \therefore \quad &\left(\frac{d}{dp}\right)_\tau\left[JK\right] = \left(\frac{d}{d\tau}\right)_p\left[-JKA\left(\frac{\tau_0}{\tau}\right)^2\right]; \end{aligned}\right\} \tag{150}$$

$$\therefore \quad K = K_0\left(\frac{\tau}{\tau_0}\right)^2 e^{\frac{m(\tau^3-\tau_0^3)}{3\tau_0^2} - mA(p-p_0)}. \tag{151}$$

This, where m is some constant, would make K vary much more than experiment shows it to do.

Supposing (148) to be true, and assuming

$$v = \frac{R\tau}{p} + F, \tag{152}$$

where F is very small.

Then

$$\begin{aligned} JKA\left(\frac{\tau_0}{\tau}\right)^2 &= \tau\left(\frac{dv}{d\tau}\right)_p - v \\ &= \tau\left[\frac{R}{p} + \left(\frac{dF}{d\tau}\right)_p\right] - \left[\frac{R\tau}{p} + F\right] \\ &= \tau\left(\frac{dF}{d\tau}\right)_p - F; \end{aligned} \tag{153}$$

$$\therefore \left(\frac{d}{d\tau}\right)_p \left(\frac{F}{\tau}\right) = JAK\frac{\tau_0^2}{\tau^4}$$

$$= JAK_0\tau^{-2}e^{\frac{m(\tau^3-\tau_0^3)}{3\tau_0^2}-mA(p-p_0)};$$

$$\therefore \frac{F}{\tau}-\frac{F_0}{\tau_0} = JAK_0\int_{\tau_0}^{\tau}\tau^{-2}e^{\frac{m(\tau^3-\tau_0^3)}{3\tau_0^2}-mA(p-p_0)}d\tau$$

$$= JAK_0e^{-m\left[\frac{\tau_0}{3}+A(p-p_0)\right]}\int_{\tau_0}^{\tau}e^{\frac{m\tau^3}{3\tau_0^2}}\frac{d\tau}{\tau^2}$$

$$= JAK_0e^{-m\left[\frac{\tau_0}{3}+A(p-p_0)\right]}\int_{\tau_0}^{\tau}\left[1+\frac{m\tau^3}{3\tau_0^2}+\&c.\right]\frac{d\tau}{\tau^2}$$

$$= JAK_0e^{-m.\left[\frac{\tau_0}{3}+A(p-p_0)\right]}\left\{\left(\frac{1}{\tau_0}-\frac{1}{\tau}\right)+\frac{m(\tau^2-\tau_0^2)}{6\tau_0^2}+\&c.\right\}$$

$$\therefore F = F_0\frac{\tau}{\tau_0}+JAK_0e^{-m\left[\frac{\tau_0}{3}+A(p-p_0)\right]}\left(\frac{\tau-\tau_0}{\tau_0}\right)\left\{1+\frac{m(\tau+\tau_0)\tau}{6\tau_0}+\&c.\right\}$$

$$\therefore v = \frac{R\tau}{p}+F_0\frac{\tau}{\tau_0}+JAK_0\frac{\tau-\tau_0}{\tau_0}e^{-m\left[\frac{\tau_0}{3}+A(p-p_0)\right]}\left[1+\frac{m(\tau+\tau_0)\tau}{6\tau_0}+\&c.\right] \quad (154)$$

which differs considerably from the formula given by Joule and Thomson, namely,

$$v = \frac{R\tau}{p}-\frac{1}{3}AJK\left(\frac{\tau_0}{\tau}\right)^2, \quad (155)$$

which they seem to have derived from (148) on the supposition of K being constant.

But if K is constant we get (133), which is inconsistent with (148), the result of the Joule-Thomson experiments.

It would appear, therefore, that the important point to be determined is whether K, for air, is or is not a function of the temperature of the air.

The result (148) of the Joule-Thomson experiments indicates that K is a function of the temperature, but the form of the function (151) obtained from this result makes K vary with the temperature *much more than it is known to do.* Hence it appears that the Joule-Thomson experiments *must be repeated,* or the mode by which (148) was deduced from them *must be scrutinized.*

CHAPTER XII.

PERFECT GASES.

ASSUMING that perfect gases are such as follow the laws of Boyle and Charles, we have for such

$$pv = Rt, \tag{158}$$

where R is a constant.

Now from (55),

$$\mu = \frac{1}{J(K-N)}\left(\frac{dv}{dt}\right)_p \cdot \left(\frac{dp}{dt}\right)_v$$

$$= \frac{1}{J(K-N)} \cdot \frac{R}{p} \cdot \frac{R}{v} \text{ from (158)}$$

$$= \frac{R}{J(K-N)\,t}. \tag{159}$$

But μ is a function of t only; $\therefore$ $K-N$ must either be constant or a function of t.

Again from (42)

$$\mu = \frac{1}{JM}\left(\frac{dp}{dt}\right)_v$$

$$\left.\begin{aligned} &= \frac{1}{JM} \cdot \frac{R}{v} \\ &= \frac{1}{JM} \cdot \frac{p}{t} \end{aligned}\right\} \text{ by (158).} \tag{160}$$

Now by definition

$$\delta E = J\delta H - p\delta v. \tag{161}$$

But by Mayer's hypothesis, practically confirmed by Joule's experiments on gases, and by the Joule-Thomson experiments on the flow of gases through porous plugs, E remains constant at constant temperatures.

Hence
$$\left(\frac{dE}{dv}\right)_t = 0.$$

Therefore (161) becomes

$$J\left(\frac{dH}{dv}\right)_t - p = \left(\frac{dE}{dv}\right)_t$$
$$= 0,$$

or
$$p = J\left(\frac{dH}{dv}\right)_t$$
$$= JM. \tag{162}$$

Consequently (160) becomes

$$\mu = \frac{1}{p} \cdot \frac{p}{t}$$
$$= \frac{1}{t}. \tag{163}$$

Hence from (159) we get

$$K - N = \frac{R}{J\mu t}$$
$$= \frac{R}{J}. \tag{164}$$

Again, from (43), (158), and (162),

$$J\left(\frac{dK}{dp}\right)_t = \left(\frac{d}{dt}\right)_p \left\{ v + JM\left(\frac{dv}{dp}\right)_t \right\}$$
$$= \left(\frac{d}{dt}\right)_p \left\{ v + p\left(-\frac{v}{p}\right) \right\}$$
$$= 0. \tag{165}$$

Hence K is a function of t only, or a constant.

Again, from (46), (162), and (42),

$$\left(\frac{dN}{dv}\right)_t = \left(\frac{dM}{dt}\right)_v - M\mu$$

$$= \frac{1}{J}\left(\frac{dp}{dt}\right)_v - M\mu$$

$$= M\mu - M\mu$$

$$= 0. \qquad (166)$$

Hence N is a function of t only, or a constant.

But, from (164), $K - N$ has a constant value. Hence it seems probable that K and N are constants. That K is so has been proved by Regnault's experiments (*Comptes Rendus*, vol. xxxvi., 1853; also *Relation des Expériences*, vol. ii.). And from (164) it follows that N must be so also.

Conversely, if K and N are constants, (163) and Mayer's hypothesis follow.

From the Table of Differential Coefficients, and from (162), (158), and (164),

$$\left(\frac{dv}{dt}\right)_\phi = -\frac{N}{M}$$

$$= -\frac{JN}{p}$$

$$= -\frac{JNv}{Rt}$$

$$= -\frac{Nv}{(K-N)\,t};$$

$$\therefore \quad \frac{1}{v}\left(\frac{dv}{dt}\right)_\phi = -\frac{N}{K-N}\cdot\frac{1}{t}. \qquad (167)$$

Integrating this between limits, we have

$$\left.\begin{aligned} &\log\left(\frac{v}{v_0}\right) = -\frac{N}{K-N}\cdot\log\left(\frac{t}{t_0}\right) \\ \text{or}\quad &\left(\frac{v}{v_0}\right)^{K-N} = \left(\frac{t_0}{t}\right)^{N} \\ \text{or}\quad &v^{K-N}.\ t^{N} = v_0^{K-N}.\ t_0 \\ &\qquad = \text{a function of } \phi. \end{aligned}\right\} \quad (168)$$

Again, from the Table of Differential Coefficients, and (162) and (163),

$$\left(\frac{dp}{dt}\right)_\phi = \frac{JKM\mu}{K-N}$$

$$= \frac{pK}{(K-N)\,t};$$

$$\therefore\quad \frac{1}{p}\left(\frac{dp}{dt}\right)_\phi = \frac{K}{K-N}\cdot\frac{1}{t}. \quad (169)$$

Hence by integration

$$\left.\begin{aligned} &\log\left(\frac{p}{p_0}\right) = \frac{K}{K-N}\log\left(\frac{t}{t_0}\right) \\ \text{or}\quad &\left(\frac{p}{p_0}\right)^{K-N} = \left(\frac{t}{t_0}\right) \\ \text{or}\quad &\frac{p^{K-N}}{t^{K}} = \frac{p_0^{K-N}}{t_0^{K}} \\ &\qquad = \text{function of } \phi. \end{aligned}\right\} \quad (170)$$

Again, from the Table of Differential Coefficients, and from (162), (163), (158), and (164),

$$\left(\frac{dp}{dv}\right)_\phi = -\frac{JKM^2\mu}{N(K-N)}$$

$$= -\frac{Kp^2}{JN(K-N)\,t}$$

$$= -\frac{RKp}{JN(K-N)\,v}$$

$$= -\frac{Kp}{Nv};$$

$$\therefore \quad \frac{1}{p}\left(\frac{dp}{dv}\right)_\phi = -\frac{K}{N}\cdot\frac{1}{v}. \tag{171}$$

Integrating, we get

$$\left.\begin{aligned} &\log\left(\frac{p}{p_0}\right) = -\frac{K}{N}\log\frac{v}{v_0} \\ \text{or}\quad &\left(\frac{p}{p_0}\right)^N = \left(\frac{v_0}{v}\right)^K \\ \text{or}\quad &p^N v^K = p_0{}^N.\, v_0{}^K \\ &\qquad = \text{a function of } \phi. \end{aligned}\right\} \tag{172}$$

Again, from Table of Differential Coefficients, and from (162), (158), (163), and (164),

$$\begin{aligned} \delta\phi &= \left(\frac{d\phi}{dp}\right)_v \delta p + \left(\frac{d\phi}{dv}\right)_p \delta v \\ &= \frac{N}{M\mu}\, e^{-\int\mu dt}\,\delta p + \frac{JMK}{K-N}\, e^{-\int\mu dt}\,\delta v \\ &= \frac{JN}{p}\,\delta p + \frac{JK}{v} \end{aligned} \tag{173}$$

Integrating, we have

$$\left.\begin{aligned} &\phi - \phi_0 = JN\log\left(\frac{p}{p_0}\right) + JK\log\left(\frac{v}{v_0}\right) \\ \text{or}\quad &e^{\phi-\phi_0} = \left(\frac{p}{p_0}\right)^{JN}\cdot\left(\frac{v}{v_0}\right)^{JK} \\ \text{or}\quad &\frac{p^{JN}v^{JK}}{e} = \frac{p_0{}^{JN}.\, v_0{}^{JK}}{e^{\phi_0}} \\ &\qquad = \text{a constant.} \end{aligned}\right\} \tag{174}$$

But from (158),

$$\left(\frac{t}{pv}\right)^{JN} = \frac{1}{R^N} = \left(\frac{t_0}{p_0 v_0}\right)^{JN}. \tag{175}$$

Multiplying (174) by this we get

$$\left.\begin{aligned} \frac{v^{J(K-N)}\, t^{JN}}{e^{\phi}} &= \frac{v_0{}^{J(K-N)}\, t_0{}^{JN}}{e^{\phi_0}} \\ &= \text{a constant.} \end{aligned}\right\} \tag{176}$$

Also from (158),

$$\left(\frac{t}{pv}\right)^{JK} = \frac{1}{R^{JK}} = \left(\frac{t_0}{p_0 v_0}\right)^{JK}. \tag{177}$$

Multiplying (174) by this we get

$$\left.\begin{aligned} \frac{t^{JK}}{p^{J(K-N)}\, e^{\phi}} &= \frac{t_0{}^{JK}}{p_0{}^{J(K-N)}\, e^{\phi_0}} \\ &= \text{a constant.} \end{aligned}\right\} \tag{178}$$

Again, from the Table of Differentials, and from (162), (158), and (164),

$$\begin{aligned} \delta E &= \left(\frac{dE}{dv}\right)_p \delta v + \left(\frac{dE}{dp}\right)_v \delta p \\ &= \frac{JMK + (N-K)p}{K-N}\,\delta v + \frac{N}{M\mu}\,\delta p \\ &= \frac{pN}{K-N}\,\delta v + \frac{JNt}{p}\,\delta p \\ &= \frac{pN}{K-N}\,\delta v + \frac{JNv}{R}\,\delta p \\ &= \frac{pN}{K-N}\,\delta v + \frac{Nv}{K-N}\,\delta p \\ &= \frac{N}{K-N}\,(p\delta v + v\delta p) \\ &= \frac{N}{K-N}\,\delta(pv); \end{aligned} \tag{179}$$

$$\left.\begin{aligned} \therefore \quad E - E_0 &= \frac{N}{K-N}(pv - p_0 v_0) \\ &= JN(t - t_0). \end{aligned}\right\} \qquad (180)$$

From (180) it is evident that *for a perfect gas Isotherms are Isenergics.*

Newton's theoretical velocity of sound in a gas is

$$V_\nu = \sqrt{g \cdot \frac{p}{\rho}}, \qquad (181)$$

where p and ρ denote the pressure and density of the gas.

This is found to be considerably less than the observed velocity.

This result Newton derived from supposing Boyle's law to hold for the gas, and thus neglecting the variations of temperature produced by the sound waves.

Laplace, assuming these variations of temperature to be isentropic, or that the variations are so rapid that there is no sensible radiation or conduction to the surrounding air or other neighbouring bodies, proved the velocity to be

$$V_\lambda = \sqrt{\frac{K}{N} \cdot g \cdot \frac{p}{\rho}}. \qquad (182)$$

This is found to agree very closely with the observed velocity.

From (181) and (182) we get

$$\frac{K}{N} = \left(\frac{V_\lambda}{V_\nu}\right)^2. \qquad (183)$$

For air, and other nearly perfect gases, the value of this has been found to be 1·41.

Hence

$$\frac{K}{N} = 1{\cdot}41. \qquad (184)$$

Substituting this in (174), (176), and (178), we get, for air, &c. (supposing them perfect gases),

$$\left.\begin{aligned} &\frac{p \cdot v^{1\cdot41}}{e^{\frac{\phi}{JN}}} = \text{a constant,} \\ &\frac{v^{\cdot41}\, t}{e^{\frac{\phi}{JN}}} = \text{a constant,} \\ \text{and} \quad &\frac{t^{1\cdot41}}{p^{\cdot41}\, e^{\frac{\phi}{JN}}} = \text{a constant.} \end{aligned}\right\} \tag{185}$$

If a perfect gas be compressed at constant temperature from volume V to volume V', and if H be the heat emitted by it, then

$$H = \int_{V'}^{V} M dv \text{ by definition of } M.$$

$$= \int_{V'}^{V} \frac{1}{J\mu} \left(\frac{dp}{dt}\right)_v dv \text{ by (42)}$$

$$= \int_{V'}^{V} \frac{1}{J\mu} \cdot \frac{R}{v}\, dv \text{ by (158)}$$

$$= \frac{R}{J\mu} \log\left(\frac{V}{V'}\right). \tag{186}$$

Again, if W denote the work expended in compressing the gas, then

$$W = \int_{V'}^{V} p\, dv$$

$$= \int_{V'}^{V} \frac{Rt}{v}\, dv$$

$$= Rt \log\left(\frac{V}{V'}\right). \tag{187}$$

From (186) and (187) we get

$$\left.\begin{aligned} \frac{W}{H} &= J\mu t \\ \text{or} \qquad W &= JH\mu t. \end{aligned}\right\} \tag{188}$$

If it be assumed that

$$\mu = \frac{1}{t}, \tag{189}$$

then (188) becomes

$$W = J \,.\, H. \tag{190}$$

That is, the work done in compressing a portion of gas at constant temperature from one volume to another is dynamically equivalent to the heat emitted by the gas during this compression.

This is *Mayer's principle*, which is thus shown to follow from the assumptions (158) and (189).

If W denote the work done during adiabatic or isentropic compression of a gas from volume V to V', we have from (185)

$$p \,.\, v^{1\cdot41} = C; \tag{191}$$

and

$$\begin{aligned} \therefore \quad W &= \int_{V'}^{V} p dv \\ &= \int_{V'}^{V} \frac{C}{v^{1\cdot41}} dv \\ &= \frac{C}{\cdot41} \left\{ \frac{1}{(V')^{\cdot41}} - \frac{1}{V^{\cdot41}} \right\}. \end{aligned} \tag{192}$$

Substituting in this from (191) we get

$$\begin{aligned} W &= \frac{p'V' - pV}{\cdot41} \\ &= \frac{R(t' - t)}{\cdot41} \end{aligned}$$

$$= \frac{Rt}{\cdot 41}\left\{\frac{t'}{t} - 1\right\}$$

$$= \frac{Rt}{\cdot 41}\left\{\left(\frac{V}{V'}\right)^{\cdot 41} - 1\right\} \text{ from (185).} \qquad (193)$$

This result may be obtained thus:—

$$W = E' - E$$

$$= JN(t' - t) \text{ from (180)}$$

$$= JNt\left(\frac{t'}{t} - 1\right)$$

$$= JNt\left\{\left(\frac{V}{V'}\right)^{\cdot 41} - 1\right\} \text{ from (191).} \qquad (194)$$

But from (164),

$$JN = JK - R$$

$$= 1\cdot 41\, JN - R \text{ from (184);}$$

$$\therefore \quad JN = \frac{R}{\cdot 41}. \qquad (195)$$

Hence (194) becomes

$$W = \frac{Rt}{\cdot 41}\left\{\left(\frac{V}{V'}\right)^{\cdot 41} - 1\right\}. \qquad (196)$$

If W denote the work done by a perfect (or reversible) air-engine working between the temperatures S and R, and if H denote the heat taken in at temperature S, and H' the quantity given out at temperature R.

Then $W = J(H - h)$ from First Law.

$$= J\left\{\int_{\phi'}^{\phi}\left[M\left(\frac{dv}{d\phi}\right)_t\right]_{t=S} d\phi - \int_{\phi'}^{\phi}\left[M\left(\frac{dv}{d\phi}\right)_t\right]_{t=R} d\phi\right\}$$

$$= \left\{\int_{\phi'}^{\phi}\left[e^{\int \mu dt}\right]_{t=S} d\phi - \int_{\phi'}^{\phi}\left[e^{\int \mu dt}\right]_{t=R} d\phi\right\} \text{ from Table}$$

$$= \left\{ \left[e^{\int \mu dt} \right]_{t=S} - \left[e^{\int \mu dt} \right]_{t=R} \right\} (\phi - \phi')$$

$$= e^{\int \mu dt} (\phi - \phi') \left\{ 1 - \frac{\left[e^{\int \mu dt} \right]_{t=R}}{\left[e^{\int \mu dt} \right]_{t=S}} \right\}$$

$$= JH \left\{ 1 - e^{-\int_R^S \mu dt} \right\}. \qquad (197)$$

This was first proved by Thomson.

If $\mu = \frac{1}{t}$ this becomes

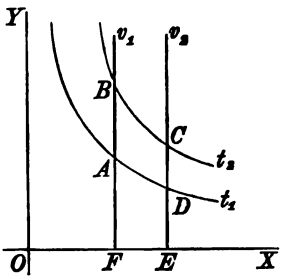
$$W = JH \left\{ 1 - \frac{R}{S} \right\}$$

$$= JH \left(\frac{S - R}{S} \right). \qquad (198)$$

This is true for all reversible engines if S and R denote the absolute temperatures of the source and refrigerator.

In Stirling's air-engine the cycle of changes is an Isothermomegacycle or a (t, v) cycle.

Let t_1 and t_2 be the two bounding isotherms, and v_1 and v_2 the two bounding isomegs.



The working body of air being initially of volume v_1 and temperature t_2 (this state is indicated by B on the diagram), is allowed to expand at temperature t_2 until its volume becomes v_2.

This change is indicated by BC; the external work done during the change is represented by the area $BCEF$, and the heat absorbed by the working air is denoted by $\int_{v_1}^{v_2} M_{t_2} dv$.

In the second operation to which the working air is subjected, it is passed through between a set of metal plates called a regenerator, which robs it of some of its heat, during which the volume of the air remains constantly v_2, and its temperature falls from t_2 to t_1.

This operation is indicated by CD on the diagram, the external work done is zero, and the heat parted with to the regenerator is $\int_{t_1}^{t_2} N_{v_2}\, dt$.

In the third operation, represented by DA, the air is compressed at temperature t_1 from volume v_2 to volume v_1, during which it has external work, represented by $ADEF$, done upon it, and it emits heat, of amount $\int_{v_1}^{v_2} M_{t_1}\, dv$, to the refrigerator.

During this fourth operation, represented by AB, the air is caused to repass through the regenerator, during which its volume remains v_1, and its temperature rises from t_1 to t_2.

No external work is done by or on the air during this operation, but heat of amount $\int_{t_1}^{t_2} N_{v_1}\, dt$ is received by it from the regenerator.

The algebraic sum of the quantities of heat received by the working air during this cycle is

$$\int dH = \int_{v_1}^{v_2} M_{t_2}\, dv - \int_{t_1}^{t_2} K_{v_2}\, dt - \int_{v_1}^{v_2} M_{t_1}\, dv + \int_{t_1}^{t_2} K_{v_1}\, dt.$$

But for air K is constant, and $JM = p$. Hence the above becomes

$$\int dH = \frac{1}{J}\int_{v_1}^{v_2} (p_{t_2} - p_{t_1}) dv$$

$$= \frac{R}{J}\int_{v_1}^{v_2} \frac{t_2 - t_1}{v}\, dv$$

$$= \frac{R\,(t_2 - t_1)}{J} \log \frac{v_2}{v_1};$$

and by the First Law the work done is

$$W = J \int dH$$

$$= R\,(t_2 - t_1) \log \left(\frac{v_2}{v_1}\right). \qquad (199)$$

It is worthy of remark that this is the same as (198). For if H_{t_2} denote the heat received at temperature t_2,

$$H_{t_2} = \frac{R\,t_2}{J} \log \left(\frac{v_2}{v_1}\right). \qquad (200)$$

Hence (199) becomes

$$W = JH_{t_2} \cdot \frac{t_2 - t_1}{t_2}. \qquad (201)$$

This will be the case in all engines where a regenerator is used, that is, where one pair of isograms of the isograph are *adiabatic*, as in the present case, where the heat taken in during the operation represented by AB is equal to the heat emitted during the operation represented by CD.

Hence all reversible engines of this sort are equally efficient with Carnot's.

CHAPTER XIII.

VAPOURS NOT IN CONTACT WITH THEIR LIQUIDS.

ALTHOUGH much is known of superheated vapours, no theoretical law has yet been found connecting their pressure, volume, and temperature, which has received general acceptance among scientific or practical men.

A theoretical formula has been given by Rankine founded on what he calls his Centrifugal Theory of Elasticity.

The formula is

$$\frac{pv}{p_0 v_0} = \frac{\tau}{\tau_0} - A_0 - \frac{A_1}{\tau} - \frac{A_2}{\tau^2} - \&c., \qquad (202)$$

where A_0, A_1, A_2, &c., are functions of the density $\frac{1}{v}$, which in the case of air and carbonic acid gas have been found to be sensibly proportional to $\frac{1}{v}$.

Hence putting

$$\frac{B_0}{v}, \frac{B_1}{v}, \frac{B_2}{v}, \&c.,$$

for A_0, A_1, A_2, &c., (202) becomes for these

$$\frac{pv}{p_0 v_0} = \frac{\tau}{\tau_0} - \frac{1}{v}\left\{B_0 + \frac{B_1}{\tau} + \frac{B_2}{\tau^2} + \&c.\right\} \qquad (203)$$

where B_0, B_1, B_2, &c., are constants.

Joule and Thomson have made use of a similar formula,

$$pv = R\tau - \frac{1}{v}\left(a - \frac{\beta}{\tau} + \frac{\gamma}{\tau^2}\right). \qquad (204)$$

These have been found to be very consistent with tabulated results of observation.

Various other formulæ have been proposed, partly theoretical and partly empirical, such as

$$pv = R\tau - Ap^{\frac{1}{4}}, \tag{205}$$

$$pv = R\tau - Av^{-n}, \tag{206}$$

$$pv = R\tau - \frac{A}{pv^{\frac{3}{2}}}, \tag{207}$$

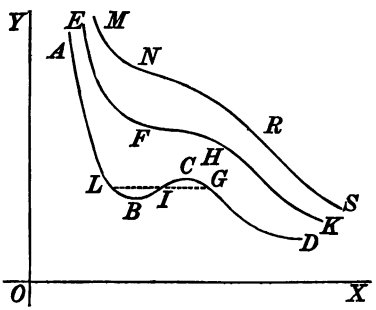
proposed by Zeuner, Hirn, and Ritter, respectively, which all give results closely concordant with tabulated results.

For certain reasons, which will appear, I would suggest a form which is a slight modification of those of Rankine, and Joule and Thomson.

The form is

$$pv = R\tau \left\{ 1 - \frac{C}{v\tau} + \frac{1}{v^2}\left[\frac{C_1}{\tau} + \frac{C_2}{\tau^2} + \&c.\right]\right\} \tag{208}$$

Professor James Thomson has suggested that isotherms, for temperatures below the critical temperature, are only *apparently* discontinuous like $ALGD$, and that their true form is somewhat like the curve $ABCD$, with maximum and minimum ordinates at C and B. Hence, corresponding to any ordinate intermediate in length between those of C and B, there will be three abscissæ, namely, those of the points L, I, G, which would indicate that the fluid at the temperature corresponding to this isotherm, and under the pressure corresponding to the common



ordinate of the points L, I, G can exist in three different states: the liquid state, denoted by L, the gaseous state, by G, and an intermediate state, by I.

The intermediate state will be unstable, because the pressure and volume increase or diminish simultaneously, and any very slight disturbance would cause the substance to change into the liquid or gaseous state, indicated by L and G. Hence, at the temperature and pressure in question, the substance will exist in two portions, one in the liquid state indicated by L, and the other in the gaseous state, indicated by G. This explains the existence of a vapour in contact with its liquid.

It is also known that the critical isotherm, $EFHK$, and isotherms above it, such as $MNRS$, have portions FH and NR which are concave towards the axes, while the portions on both sides of this are convex.

Professor J. Thomson's suggestion and these facts will be satisfied if the following conditions are satisfied:—

For an isotherm below the critical one there must be two points B and C, for which

$$\frac{dp}{dv} = 0. \tag{209}$$

And for the critical isotherm, for any isotherm below it, and for the isotherms for some distance above it, there must be two points where

$$\frac{d^2p}{dv^2} = 0, \tag{210}$$

that is, points such as F, H, N, R, where the curvature changes from concavity to convexity, or the reverse.

These conditions, as well as the further condition that at and above a certain temperature, τ_2, an isotherm has no part

concave towards the axes, will be satisfied by (208) if, denoting the critical temperature by τ_1,

$$C_1 = \frac{C^2}{24(\tau_2 - \tau_1)}, \tag{211}$$

and

$$C_2 = \frac{(8\tau_2 - 9\tau_1)\, C^2}{24(\tau_2 - \tau_1)}; \tag{212}$$

and C_3, C_4, &c., are each zero.

Hence (208) becomes

$$pv = R\tau \left\{ 1 - \frac{C}{v\tau} + \frac{C^2}{24v^2(\tau_2 - \tau_1)} \left[\frac{1}{\tau} - \frac{9\tau_1 - 8\tau_2}{\tau^2} \right] \right\}. \tag{213}$$

For carbonic acid gas,

$$\left.\begin{aligned} \tau_1 &= 274 + 31 = 305^\circ \text{ C.}, \\ \text{and} \quad \tau_2 &= 274 + 48 = 322^\circ \text{ C.} \end{aligned}\right\} \tag{214}$$

Hence (213) becomes

$$pv = R\tau \left\{ 1 - \frac{C}{v\tau} + \frac{C^2}{408v^2} \left[\frac{1}{\tau} - \frac{169}{\tau^2} \right] \right\}. \tag{215}$$

If we put τ for t and $\frac{1}{\tau}$ for μ in (43) and (46), we get

$$\begin{aligned} J\left(\frac{dK}{dp}\right)_\tau &= \left(\frac{d}{d\tau}\right)_p \left\{ JM\left(\frac{dv}{dp}\right)_\tau + v \right\} \\ &= \left(\frac{d}{d\tau}\right)_p \left\{ \tau\left(\frac{dp}{d\tau}\right)_v \left(\frac{dv}{dp}\right)_\tau + v \right\} \text{ from (42)} \\ &= \left(\frac{d}{d\tau}\right)_p \left\{ -\tau\left(\frac{dv}{d\tau}\right)_p + v \right\} \text{ from (1)} \\ &= -\tau\left(\frac{d^2v}{d\tau^2}\right)_p; \end{aligned} \tag{216}$$

and

$$J\left(\frac{dN}{dv}\right)_\tau = J\left(\frac{dM}{d\tau}\right)_v - \frac{JM}{\tau}$$

$$= \left(\frac{d}{d\tau}\right)_v \left[\tau \left(\frac{dp}{d\tau}\right)_v\right] - \left(\frac{dp}{d\tau}\right)_v \text{ from (42)}$$

$$= \tau \left(\frac{d^2p}{d\tau^2}\right)_v \tag{217}$$

Now from Zeuner's formula (205),

$$\left(\frac{d^2v}{d\tau^2}\right)_p = 0. \tag{218}$$

Hence (216) becomes

$$\left(\frac{dK}{dp}\right)_\tau = 0. \tag{219}$$

Therefore K is either constant or a function of τ only.

Again, from Hirn's formula (206),

$$\left(\frac{d^2p}{d\tau^2}\right)_v = 0. \tag{220}$$

Hence (217) becomes

$$\left(\frac{dN}{dv}\right)_\tau = 0. \tag{221}$$

Therefore N is either constant or a function of τ only.

From all the equations (203)–(213) it appears that (218)–(221) are either exactly true or nearly so.

Now
$$\delta\phi = \left(\frac{d\phi}{dp}\right)_\tau \delta p + \left(\frac{d\phi}{d\tau}\right)_p \delta\tau$$

$$= -\frac{K-N}{M}\,\delta p + \frac{JK}{\tau}\,\delta\tau \text{ from the Table}$$

$$= -\left(\frac{dv}{d\tau}\right)_p \delta p + \frac{JK}{\tau}\,\delta\tau \quad \text{,, ,, ,,}$$

$$= -\frac{R}{p}\,\delta p + \frac{JK}{\tau}\,\delta\tau \text{ from (205).}$$

Integrating this we get

$$\phi - \phi_0 = R \log\left(\frac{p_0}{p}\right) + J\int_{\tau_0}^{\tau} \frac{K}{\tau}\, d\tau. \qquad (222)$$

If K is constant, this becomes

$$\phi - \phi_0 = R \log\left(\frac{p_0}{p}\right) + JK \log \frac{\tau}{\tau_0}. \qquad (223)$$

Again,

$$\begin{aligned}
\delta\phi &= \left(\frac{d\phi}{dv}\right)_\tau \delta v + \left(\frac{d\phi}{d\tau}\right)_v \delta\tau \\
&= \frac{JM}{\tau}\,\delta v + \frac{JN}{\tau}\,\delta\tau \text{ from Table} \\
&= \left(\frac{dp}{d\tau}\right)_v \delta v + \frac{JN}{\tau}\,\delta\tau \text{ from (42)} \\
&= \frac{R}{v}\,\delta v + \frac{JN}{\tau}\,\delta\tau \text{ from (206).}
\end{aligned}$$

Integrating, we get

$$\phi - \phi_0 = R \log\left(\frac{v}{v_0}\right) + J\int_{\tau_0}^{\tau} \frac{N}{\tau}\, d\tau; \qquad (224)$$

or if N is constant,

$$\phi - \phi_0 = R \log\left(\frac{v}{v_0}\right) + JN \log\left(\frac{\tau}{\tau_0}\right). \qquad (225)$$

Again,

$$\begin{aligned}
\delta E &= \left(\frac{dE}{d\tau}\right)_v \delta\tau + \left(\frac{dE}{dv}\right)_\tau \delta v \\
&= JN\delta\tau + (JM - p)\,\delta v \\
&= JN\delta\tau + \left[\tau\left(\frac{dp}{d\tau}\right)_v - p\right]\delta v \text{ by (42)} \\
&= JN\delta\tau + \left[\tau \cdot \frac{R}{v} - p\right]\delta v \text{ by (206)} \\
&= JN\delta\tau + Av^{-(n+1)}\,\delta v \text{ by (206).}
\end{aligned}$$

Integrating

$$E - E_0 = J\int_{\tau_0}^{\tau} N dt - A\frac{v^{-n} - v_0^{-n}}{n}. \qquad (226)$$

If N be constant, this becomes

$$E - E_0 = JN(\tau - \tau_0) - \frac{A(v^{-n} - v_0^{-n})}{n}. \qquad (227)$$

In the proof of (197) it was shown that, in a finite isothermentropicycle, whatever be the nature of the working body, if W denote the work,

$$W = J\left\{\left[e^{\int \mu dt}\right]_{t=S} - \left[e^{\mu dt}\right]_{t=\bar{R}}\right\}(\phi - \phi_0), \qquad (228)$$

which, if $t = \tau$ = absolute temperature, becomes

$$W = J(S - \bar{R})(\phi - \phi_0). \qquad (229)$$

But if in (224) we put $\tau = \tau_0$, it becomes

$$\phi - \phi_0 = R\log\frac{v}{v_0}. \qquad (230)$$

Hence from this and (229) we get

$$W = R(S - R)\log\left(\frac{v}{v_0}\right), \qquad (231)$$

where v_0 and v are the volumes of the working body at the beginning and end of the expansion at temperature S, or they are the volumes at the end and beginning of the compression at temperature $\bar{R}$.

This would also be true for a perfect gas working through the same cycle.

What follows, although not a complete cycle of operations, is the ideal of the set of operations which take place in a cylinder in which high pressure dry steam works expansively.

First.—Let steam of temperature t_1, pressure p_1, and volume v_1 be admitted to the cylinder.

Second.—Let the steam expand adiabatically to volume v_2, the temperature and pressure changing to t_2 and p_2.

Third.—Let the steam be admitted to the condenser, and let it be driven into the condenser by the return stroke of the piston with a pressure p_3 through the volume v_2.

The work done in the first operation is $p_1 v_1$.

In the second operation the work done is $E_1 - E_2$, where E_1 and E_2 denote the intrinsic energy of the admitted steam at the beginning and end of this operation.

During the third operation the piston, exerting a pressure p_3 through a volume v_2, does work of amount $p_3 v_2$.

Note that, at the moment of admission to the condenser, the pressure suddenly falls from p_2 to p_3, but no work is done.

From this it is evident that during a *double stroke* of the piston the work done on *one face* of the piston by the steam has for its algebraic sum

$$\left.\begin{aligned} W &= p_1 v_1 + E_1 - E_2 - p_3 v_2 \\ &= p_1 v_1 + JN(\tau_1 - \tau_2) - \frac{A(v_1^{-n} - v_2^{-n})}{n} - p_3 v_2 \text{ by (227).} \end{aligned}\right\} \quad (232)$$

But since τ_2 is not known, it ought to be expressed in terms of the known quantities, thus :—

During the second operation ϕ is constant. Hence $\phi_1 = \phi_2$. Therefore from (225)

$$\begin{aligned} 0 &= \phi_2 - \phi_1 \\ &= R \log\left(\frac{v_2}{v_1}\right) + JN \log \frac{\tau_2}{\tau_1}; \end{aligned}$$

$$\therefore \quad \tau_2 = \tau_1 \left(\frac{v_2}{v_1}\right)^{-\frac{R}{JN}}. \qquad (233)$$

Substituting this in (232) we get

$$W = JN\tau_1\left[1-\left(\frac{v_2}{v_1}\right)^{-\frac{R}{JN}}\right]+p_1v_1-p_3v_2-\frac{A\left(v_1^{-n}-v_2^{-n}\right)}{n}. \quad (234)$$

But for steam Rankine gives

$$\frac{R}{JN} = \gamma - 1 = \cdot 304. \quad (235)$$

Hence we have

$$\left.\begin{aligned}
W &= JN\tau_1\left\{1-\left(\frac{v_2}{v_1}\right)^{-\cdot 304}\right\}+p_1v_1-p_3v_2-\frac{A\left(v_1^{-n}-v_2^{-n}\right)}{n}\\
&= \frac{R\tau_1}{\cdot 304}\left\{1-\left(\frac{v_2}{v_1}\right)^{-\cdot 304}\right\}+p_1v_1-p_3v_2-\frac{A\left(v_1^{-n}-v_2^{-n}\right)}{n}\\
&= \frac{p_1v_1-Av_1^{-n}}{\cdot 304}\left\{1-\left(\frac{v_2}{v_1}\right)^{-\cdot 304}\right\}+p_1v_1-p_3v_2-\frac{A\left(v_1^{-n}-v_2^{-n}\right)}{n}\\
&= p_1v_1\left\{4\cdot 29-3\cdot 29\left(\frac{v_2}{v_1}\right)^{-\cdot 304}\right\}-p_3v_2\\
&\qquad -A\left\{3\cdot 29\left(1-\left(\frac{v_2}{v_1}\right)^{-\cdot 304}\right)v_1^{-n}+\frac{v_1^{-n}-v_2^{-n}}{n}\right\}
\end{aligned}\right\} (236)$$

If we assume, as Rankine does, that

$$pv = R\tau; \quad (237)$$

and therefore that $A = 0$, (236) becomes

$$W = p_1v_1\left\{4\cdot 29-3\cdot 29\left(\frac{v_2}{v_1}\right)^{-\cdot 304}\right\}-p_3v_2, \quad (238)$$

which is the same as Rankine's formula (4), § 297 of his treatise on the "Steam Engine," in which he uses r for $\frac{v_2}{v_1}$.

Rankine's formula is sufficiently accurate for practical purposes.

Of course it is evident that $2W$ is the whole external work done in a double stroke.

Again, let a steam engine be worked as follows:—

First.—Let high-pressure steam of volume v_1, temperature t_1, and pressure p_1 be admitted to the cylinder on one side of the piston.

Second.—Let this steam be allowed to expand *isothermally* to volume v_2 and pressure p_2.

Third.—Communication with the condenser being opened, let the steam be driven into the condenser by the return stroke of the piston against a pressure p_3 through the volume v_2.

Then the work done by the steam on the piston during the first operation will be $p_1 v_1$.

During the second operation the work done by the steam on the piston will be

$$\int_{v_1}^{v_2} p_{t_1} dv = \int_{v_1}^{v_2} \left[\frac{R\tau_1}{v} - Av^{-(n+1)} \right] dv$$

$$= R\tau_1 \log \left(\frac{v_2}{v_1} \right) + \frac{A\left(v_2^{-n} - v_1^{-n}\right)}{n}.$$

During the third operation the work done by the piston on the steam will be $p_3 v_2$.

Hence the algebraic sum of the quantities of work done by the steam on one face of the piston during a double stroke will be

$$W = p_1 v_1 + R\tau_1 \log \frac{v_2}{v_1} + \frac{A\left(v_2^{-n} - v_1^{-n}\right)}{n} - p_3 v_2. \qquad (239)$$

This becomes the same as Rankine's result if $pv = R\tau$, *i.e.* if $A = 0$.

His result is

$$\left.\begin{aligned} W &= p_1 v_1 - p_3 v_2 + R\tau_1 \log \frac{v_2}{v_1} \\ &= p_1 v_1 \left[1 + \log \frac{v_2}{v_1}\right] - p_3 v_2 \\ &= p_1 v_1 \left[1 + \log r\right] - p_3 r v_1, \end{aligned}\right\} \qquad (240)$$

[see Rankine's "Steam Engine," § 298, equation (1),]

$$\text{where } r = \frac{v_2}{v_1}.$$

In Siemen's "Regenerative Steam Engine" the series of changes undergone by the steam in a double stroke is the same as this last, except that the regenerator economises heat by communicating to the steam entering the cylinder the heat received by it from the steam which immediately before left the cylinder, and thus increases the efficiency of the engine.

To compare the efficiency of this engine with a regenerator with that of one without a regenerator,

$$\frac{\text{efficiency with}}{\text{efficiency without}} = \frac{\dfrac{W}{J(H-h_2)+p_1 v_1 \log r}}{\dfrac{W}{J(H_1-h_2)+p_1 v_1 \log r}}$$

$$= \frac{J(H_1-h_2)+p_1 v_1 \log r}{J(H-h_2)+p_1 v_1 \log r},$$

where h_2 = heat required to raise 1 lb. of water at τ_0 to τ_2;

H_1 = „ to convert „ of temp. τ_0 into steam at temp. τ_1 and pressure p_1;

H = heat required to convert 1 lb. of water at τ_0 into steam at temperature τ (the temperature of the boiler) and pressure p_1.

If it be assumed that the relation between p, t, and ϕ is the same for super-heated steam as for gases, that is, if

$$\phi - \phi_0 = K\left\{\log\frac{\tau}{\tau_0} - \frac{\gamma-1}{\gamma}\log\frac{p}{p_0}\right\} \text{ from (178)}$$

$$= K\log\frac{\tau}{\tau_0} - (K-N)\log\frac{p}{p_0}, \tag{243}$$

where γ, K, and N have constant values different from those of gases.

Differentiating this, we get

$$\left(\frac{d\phi}{dp}\right)_t = -\frac{K-N}{p}. \tag{244}$$

But from the Table of Differential Coefficients,

$$\left(\frac{d\phi}{dp}\right)_t = -\frac{K-N}{JM\mu}e^{-\int\mu dt}$$

$$= -\frac{K-N}{JM}, \tag{245}$$

if $t = \tau$ and $\mu = \frac{1}{\tau}$.

Comparing (244) and (245) we get

$$p = JM \tag{246}$$

$$= \frac{1}{\mu}\left(\frac{dp}{dt}\right)_v \text{ from (42)}$$

$$= \tau\left(\frac{dp}{d\tau}\right)_v, \tag{247}$$

if $t = \tau$ and $\mu = \frac{1}{\tau}$.

Integrating (247) we get

$$\frac{p}{\tau} = f(v). \tag{248}$$

This does not agree with any of the forms (202)–(213), but it is possible that it may be made consistent with the results of experiment by giving some special form to the function $f(v)$.

CHAPTER XIV.

LATENT HEAT.

If the working body consist of two portions of the same substance in different states, the fundamental equations assume peculiar forms.

Let the working body consist of x units of a substance in a higher state, and $1-x$ units of the same substance in a lower state.

Let p and t, the pressure and temperature, be uniform throughout the body.

Let V_1 and V_2 denote the volumes of unit mass of the substance in these two states, and let v denote the volume of the body.

Hence $$v = V_1 x + V_2 (1 - x). \tag{249}$$

Again, if λ denote the latent heat of the higher form of the substance,

$$\left(\frac{dH}{dx}\right)_t = \lambda. \tag{250}$$

Lastly, if c_1 and c_2 denote the specific heats of the substance in the higher and lower forms,

$$\left(\frac{dH}{dt}\right)_x = c_1 x + c_2 (1 - x). \tag{251}$$

Let now the body go through an elementary cycle of changes having for its isograph the figure bounded by the lines (isograms) $\alpha = t, \quad \beta = x,$

and $\alpha + \delta\alpha = t + \delta t, \quad \beta + \delta\beta = x + \delta x;$

$$\therefore \quad \left(\frac{dH}{d\alpha}\right)_\beta = \left(\frac{dH}{dt}\right)_x = c_1 x + c_2(1-x),$$

$$\left(\frac{dH}{d\beta}\right)_\alpha = \left(\frac{dH}{dx}\right)_t = \lambda,$$

$$\left(\frac{d}{d\beta}\right)_\alpha \left(\frac{dH}{d\alpha}\right) = \left(\frac{d}{dx}\right)_t \left[c_1 x + c_2(1-x)\right] = c_1 - c_2,$$

$$\left(\frac{d}{d\alpha}\right)_\beta \left(\frac{dH}{d\beta}\right)_\alpha = \left(\frac{d\lambda}{dt}\right)_x = \frac{d\lambda}{dt},$$

since λ is a function of t only.

Hence (24) and (39) become

$$J\left\{\frac{d\lambda}{dt} - (c_1 - c_2)\right\} = \left(\frac{dp}{dt}\right)_v \left(\frac{dv}{dx}\right)_t, \tag{252}$$

and

$$\frac{\dfrac{d\lambda}{dt} - (c_1 - c_2)}{\lambda} = \mu. \tag{253}$$

But from (249)

$$\left(\frac{dv}{dx}\right)_t = V_1 - V_2. \tag{254}$$

Hence (252) becomes

$$J\left\{\frac{d\lambda}{dt} - (c_1 - c_2)\right\} = (V_1 - V_2)\left(\frac{dp}{dt}\right)_v. \tag{255}$$

From (253) and (255) we get

$$J\lambda\mu = (V_1 - V_2)\left(\frac{dp}{dt}\right)_v. \tag{256}$$

Now since p is a function of t only,

$$\left(\frac{dp}{dt}\right)_\phi = \left(\frac{dp}{dt}\right)_v = \left(\frac{dp}{dt}\right). \tag{257}$$

From this and (256) we get

$$\left(\frac{dt}{dp}\right)_\phi = \frac{V_1 - V_2}{J\lambda\mu}. \tag{258}$$

Again,

$$\left(\frac{d\lambda}{dp}\right)_\phi = \frac{\left(\frac{d\lambda}{dt}\right)_\phi}{\left(\frac{dp}{dt}\right)_\phi}$$

$$= \frac{\left(\frac{d\lambda}{dt}\right)}{\left(\frac{dp}{dt}\right)} \quad \text{since } p \text{ and } \lambda \text{ are both functions of } t \text{ only}$$

$$= \frac{\lambda\mu + (c_1 - c_2)}{\frac{J\lambda\mu}{V_1 - V_2}} \quad \text{from (253), (256), and (257)}$$

$$= \frac{V_1 - V_2}{J}\left\{1 + \frac{c_1 - c_2}{\lambda\mu}\right\}. \tag{259}$$

Some interesting conclusions may be drawn from these equations.

If $V_1 < V_2$, as is the case when the body consists of water and ice, (258) gives

$$\left(\frac{dt}{dp}\right)_\phi = \text{a negative quantity.} \tag{260}$$

Hence the temperature of the mixture is lowered by increase of pressure; i.e. *the freezing temperature is lowered by increase of pressure.*

This was first proved by Professor James Thomson, and he showed that it is lowered ·0075° C. by an increase of pressure of one atmosphere.

If $V_1 > V_2$, as is the case with a vapour in contact with its liquid, such as steam in contact with water, (258) gives

$$\left(\frac{dt}{dp}\right)_\phi = \text{a positive quantity.} \tag{261}$$

Hence the temperature of the mixture is raised by increase of pressure; i.e. *the boiling temperature is raised by increase of pressure.*

If $V_1 < V_2$, and $c_1 > c_2$, as is the case with water and ice (259), gives

$$\left(\frac{d\lambda}{dp}\right)_\phi = \text{a negative quantity.} \tag{262}$$

Hence *the latent heat of water is diminished by increase of pressure.*

This result is due to Clausius.

Regnault's experiments have shown that, at all temperatures tried,

$$\frac{d\lambda}{dt} + c_2 < \lambda\mu \tag{263}$$

for vapour of water.

Hence (253) becomes

$$\begin{aligned} c_1 &= \frac{d\lambda}{dt} + c_2 - \lambda\mu \\ &= \text{a negative quantity.} \end{aligned} \tag{264}$$

Rankine and Clausius simultaneously proved this.

Regnault gives the empirical formula for water:

$$c_2 = 1 + \cdot 00004\,t + \cdot 0000009\,t^2 + \&c.; \tag{265}$$

and the partly theoretical and partly empirical formula,

$$\lambda = 606\cdot 5 + \cdot 305\,t - \int_0^t c_2\,dt, \tag{266}$$

as embodying the results of his experiments.

In these two formulæ t is temperature counted from the freezing temperature.

From these Clausius deduces the approximate formula,

$$\lambda = 607 - \cdot 708t. \tag{267}$$

And from (253) deduces, on putting $\frac{1}{t}$ for μ, and then substituting $273 + t$ for t,

$$c_1 = \cdot 305 - \frac{607 - \cdot 708t}{273 + t}$$

$$\doteqdot 1\cdot 013 - \frac{800\cdot 3}{273 + t}. \tag{268}$$

From (265), (267), and (268) we see that for saturated vapour of water at all ordinary temperatures,

$$1 + \frac{c_1 - c_2}{\lambda\mu} = \text{a negative quantity.} \tag{269}$$

And since for water and vapour of water in contact $V_1 > V_2$, we derive from (259) and (269),

$$\left(\frac{d\lambda}{dp}\right)_\phi = \text{a negative quantity,} \tag{270}$$

which shows that *for all ordinary temperatures the latent heat of vapour of water is diminished by increase of pressure.*

With regard to the deductions which can be drawn from (258) Clerk Maxwell says ("Theory of Heat"):—

"Whenever the volume of the substance is, like that of water, less in the liquid than in the solid state, the effect of pressure on a vessel containing the substance partly in a liquid and partly in a solid state, is to cause some of the solid portion to melt, and to lower the temperature of the whole to the melting point corresponding to the pressure. If, on the contrary, the volume of the substance is greater in the liquid than in the solid state, the effect of pressure is to solidify some of the liquid part, and to raise the temperature to the melting point corresponding to the pressure. To

determine at once whether the volume of the substance is greater in the liquid or the solid state, we have only to observe whether solid portions of the substance sink or swim in the melted substance. If, like ice in water, they swim, the volume is greater in the solid state, and pressure causes melting and lowers the melting point. If, like sulphur, wax, and most kinds of stone, the solid substance sinks in the liquid, then pressure causes solidification and raises the melting point."

The former part of this was predicted and proved by Professor James Thomson, and confirmed experimentally by Professor (now Sir) William Thomson. The latter part was predicted by Professor William Thomson, and confirmed experimentally by Bunsen.

With regard to (264) Thomson says, in his Paper on the "Dynamical Theory of Heat":—

"From these results it appears that through the whole range of temperatures at which observations have been made, the value of h (c_1 here) is negative; and therefore if a quantity of saturated vapour be compressed in a vessel containing no liquid water, heat must be continuously abstracted from it in order that it may remain saturated as its temperature rises; and conversely, if a quantity of saturated vapour be allowed to expand in a closed vessel, heat must be supplied to prevent any part of it from becoming condensed into the liquid form as the temperature of the whole sinks. This very remarkable conclusion was first announced by Mr. Rankine, in his Paper communicated to this Society on the 4th of February last year. It was discovered independently by Clausius, and published in his Paper in Poggendorff's *Annalen* in the months of April and May of the same year. It might appear at first sight that the well-known fact that

steam rushing from a high-pressure boiler through a small orifice into the open air does not scald a hand exposed to it, is inconsistent with the proposition, that steam expanding from a state of saturation must have heat given to it to prevent any part from becoming condensed, since the steam would scald the hand unless it were dry, and consequently above the boiling point in temperature. The explanation of this apparent difficulty, given in a letter which I wrote to Joule last October, and which has since been published in the *Philosophical Magazine*, is, that the steam in rushing through the orifice produces mechanical effect which is immediately wasted in fluid friction, and consequently reconverted into heat, so that the issuing steam at the atmospheric pressure would have to part with as much heat to convert it into water at the temperature 100° as it would have had to part with to have been condensed at the high pressure and then cooled down to 100°, which for a pound of steam, initially saturated at the temperature t, is by Regnault's modification of Watt's law, $\cdot 305\ (t - 100)$ more heat than a pound of saturated steam at 100° would have to part with to be reduced to the same state; and the issuing steam must therefore be above 100° in temperature, and dry.'

Clausius proves, from Regnault's empirical formulæ for bisulphide of carbon, chloroform, bichloride of carbon, and aceton (C_5H_6O), that the vapours of these resemble the vapour of water in having negative values for their specific heats at ordinary temperatures, *i.e.* from 0° to 100° C. ("Mechanical Theory of Heat"), but that vapour of ether has a positive value. That c_1, the specific heat of saturated steam, should be negative seems startling and unnatural, but when properly understood it is not so much so.

Suppose a closed vessel of unvarying capacity to contain water and saturated steam of a certain temperature, and suppose the quantity of steam to be a pound. Let sufficient heat be added to the contents of the vessel to raise its temperature one degree. More steam is formed by the evaporation of a portion of the water; and, since this is much bulkier than the water whose evaporation gave rise to it, the original pound of steam is compressed into smaller volume, and the heat developed in it by the work of compression is more than sufficient to raise its temperature one degree, and consequently it parts with some of this heat to the water and vapour in process of formation. This quantity of heat that the pound of steam parts with, with a negative sign prefixed to it, is, *by a mathematical fiction*, said to be communicated to it, and is *called* its specific heat.

On the other hand, if saturated vapour of water is allowed to expand adiabatically (*i.e.* without taking in or giving out heat), the heat it loses due to the external work it does in overcoming external resistance to expansion is more than it must lose so as to reach the saturation density corresponding to its new temperature; consequently some of the vapour must condense, and therefore heat would require to be added to the vapour to re-evaporate the condensed portion, if it is desired to have it all in the form of saturated vapour at the new temperature.

Therefore, if saturated vapour of water is allowed to expand, heat must be communicated to it during the expansion if we wish it to remain saturated.

From (32) and because $\left(\frac{dH}{dt}\right)_\phi = 0$, we have

$$JdH = J\left(\frac{dH}{d\phi}\right)_t d\phi + J\left(\frac{dH}{dt}\right)_\phi dt$$

$$= e^{\int \mu dt} . d\phi. \qquad (271)$$

But
$$dH = \left(\frac{dH}{dx}\right)_t dx + \left(\frac{dH}{dt}\right)_x dt$$
$$= \lambda\, dx + [c_1 x + c_2(1-x)]\, dt. \qquad (272)$$

Hence from (271) and (272)
$$e^{\int \mu dt} d\phi = J\{\lambda . dx + [c_1 x + c_2(1-x)]\, dt\}$$

or
$$\left.\begin{aligned} d\phi &= J\{\lambda e^{-\int \mu dt} dx + [c_1 x + c_2(1-x)]\, e^{-\int \mu dt} . dt\} \\ &= J\{\lambda e^{-\int \mu dt} dx + x(c_1 - c_2)\, e^{-\int \mu dt} dt + c_2 e^{-\int \mu dt} dt\}. \end{aligned}\right\} \qquad (273)$$

But from (253)
$$c_1 - c_2 = \frac{d\lambda}{dt} - \lambda\mu;$$
$$\therefore \quad (c_1 - c_2)\, e^{-\int \mu dt} = \left(\frac{d\lambda}{dt} - \lambda\mu\right) e^{-\int \mu dt}$$
$$= \frac{d}{dt}\left[\lambda e^{-\int \mu dt}\right]. \qquad (274)$$

Hence (273) becomes
$$d\phi = J\left\{\lambda e^{-\int \mu dt} dx + x \frac{d}{dt}\left[\lambda e^{-\int \mu dt}\right] dt + c_2 e^{-\int \mu dt} dt\right\}$$
$$= J\left\{d\left[x\lambda e^{-\int \mu dt}\right] + c_2 e^{-\int \mu dt} dt\right\}. \qquad (275)$$

Integrating, we get
$$\phi - \phi_0 = J\left\{x\lambda e^{-\int \mu dt} - x_0 \lambda_0 e^{-\int \mu_0 dt_0} + \int_{t_0}^{t} c_2 e^{-\int \mu dt} dt\right\}. \qquad (276)$$

If we put $t = \tau$, and $\mu = \frac{1}{\tau}$, this becomes
$$\phi - \phi_0 = J\left\{\frac{x\lambda}{\tau} - \frac{x_0 \lambda_0}{\tau_0} + \int_{\tau_0}^{\tau} \frac{c_2}{\tau} d\tau\right\}. \qquad (277)$$

If c_2 is constant, as it is nearly in the case of water, (277) becomes

$$\left.\begin{aligned} &\phi - \phi_0 = J\left\{\frac{x\lambda}{\tau} - \frac{x_0\lambda_0}{\tau_0} + c_2 \log\frac{\tau}{\tau_0}\right\} \\ \text{or}\quad &\phi - J\left[\frac{x\lambda}{\tau} - c_2 \log \tau\right] = \text{a constant.} \end{aligned}\right\} \tag{278}$$

For water, $c_2 = 1$;

$$\left.\begin{aligned} \therefore\quad &\phi - \phi_0 = J\left\{\frac{x\lambda}{\tau} - \frac{x_0\lambda_0}{\tau_0} + \log\frac{\tau}{\tau_0}\right\} \\ \text{or}\quad &\phi - J\left[\frac{x\lambda}{\tau} - \log \tau\right] = \text{a constant.} \end{aligned}\right\} \tag{279}$$

If $\tau = \tau_0, \quad \lambda = \lambda_0.$

Hence for an isothermal,

$$\left.\begin{aligned} &\phi - \phi_0 = J\frac{\lambda\,(x - x_0)}{\tau} \\ \text{or}\quad &\phi - J\frac{\lambda x}{\tau} = \text{a constant.} \end{aligned}\right\} \tag{280}$$

If in (278) we put $\phi = \phi_0$, it becomes

$$\left.\begin{aligned} &\frac{x\lambda}{\tau} - \frac{x_0\lambda_0}{\tau_0} + c_2 \log\frac{\tau}{\tau_0} = 0 \\ \text{or}\quad &\frac{x\lambda}{\tau} + c_2 \log \tau = \frac{x_0\lambda_0}{\tau_0} + c_2 \log \tau_0 \\ &\qquad = \text{a constant,} \end{aligned}\right\} \tag{281}$$

which is the equation of an isentrope or adiabatic.

If $x = x_0$, (278) may be written thus:

$$\phi - J\left[\frac{x_0\lambda}{\tau} - c_2 \log \tau\right] = \phi_0 - J\left[\frac{x_0\lambda_0}{\tau_0} - c_2 \log \tau_0\right] = \text{a constant,} \tag{282}$$

which is the equation of a line whose co-ordinates represent the volume and pressure of the mixture, while the ratio of

the parts in the different states remains constant. A line of this kind is called by Zeuner a *line of constant vapour-mass*, if the two parts are liquid and vapour.

Again, by definition,

$$
\begin{aligned}
dE &= J\,.\,dH - p\,dv \\
&= J\left[\lambda dx + \left(c_1 x + c_2 \overline{1-x}\right) dt\right] - p\,dv \text{ by (272)} \\
&= J\left\{\lambda dx + \left[x\left(c_1 - c_2\right) + c_2\right] dt\right\} - p\,dv \\
&= J\lambda dx + \left\{\left[J\frac{d\lambda}{dt} - \left(V_1 - V_2\right)\frac{dp}{dt}\right] x + Jc_2\right\} dt - p\,dv \\
&\qquad \text{by (255)} \\
&= J\left\{\lambda dx + x d\lambda\right\} - \left(v - V_2\right) dp + Jc_2 dt - p\,dv \text{ by (249)} \\
&= Jd\left(\lambda x\right) - \left(v dp + p dv\right) + V_2 dp + Jc_2 dt \\
&= Jd\left(\lambda x\right) - d\left(pv\right) + V_2 dp + Jc_2 dt. \qquad (283)
\end{aligned}
$$

Hence by integration,

$$E - E_0 = J\left(\lambda x - \lambda_0 x_0\right) - \left(pv - p_0 v_0\right) + \int_{t_0}^{t}\left(Jc_2 + V_2\frac{dp}{dt}\right) dt. \quad (284)$$

If c_2 and V_2 are constant, as they are nearly in the case of water and vapour, (284) becomes

$$
\left.
\begin{aligned}
& E - E_0 = J\left(\lambda x - \lambda_0 x_0\right) - \left(pv - p_0 v_0\right) + Jc_2\left(t - t_0\right) \\
& \qquad\qquad + V_2\left(p - p_0\right) \\
\text{or}\quad & E - J\left(\lambda x + c_2 t\right) + p\left(v - V_2\right) = E_0 - J\left(\lambda_0 x_0 + c_2 t_0\right) \\
& \qquad\qquad + p_0\left(v_0 - V_2\right) = \text{a constant.}
\end{aligned}
\right\} \quad (285)
$$

If t be constant, p is also constant. Hence for an *isothermal* (285) becomes

$$E - J\lambda x + pv = \text{a constant.} \qquad (286)$$

If E is constant, (285) becomes

$$J(\lambda x + c_2 t) - p(v - V_2) = \text{a constant}, \qquad (287)$$

which is the equation of an *Isenerg.*

Substituting in (285) the value $x(V_1 - V_2)$ for $v - V_2$ found from (249), we get

$$E - J(\lambda x + c_2 t) + px(V_1 - V_2) = \text{a constant}. \qquad (288)$$

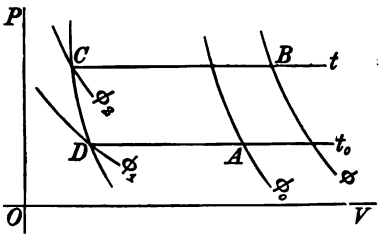
For dry saturated steam $x = 1$ and $c_2 = 1$. Hence (285) and (288) become

$$E - J(\lambda + t) + p(v - V_2) = \text{a constant}, \qquad (289)$$

and $$E - J(\lambda + t) + p(V_1 - V_2) = \text{a constant}. \qquad (290)$$

These equations may be obtained from a diagram, thus:—

Let DA and CB represent isothermals t_0 and t, and let CD be a line representing the state of the working body when entirely liquid, but about to begin to evaporate.



Let ϕ_0, ϕ, ϕ_2, ϕ_1 denote the adiabatics or isentropes through A, B, C, D.

Let also x_0 and x denote the masses of the body (whose whole mass is unity) in the form of vapour in the states indicated by A and B.

Experiment shows that in all cases of a mixture of a liquid and its vapour isothermals are also isobars. Hence DA and CB are parallel to OV, the axis of volumes.

Let the body, initially in the state A, be compressed isothermally till it is all in the liquid state. This operation is indicated by the line AD.

The heat emitted during this operation may be represented by either $\lambda_0 . x_0$, or by $\frac{1}{J}(\phi_0 - \phi_1)\, e^{\int \mu_0 dt_0}$.

Hence $$\phi_0 - \phi_1 = J\lambda_0 x_0 e^{-\int \mu_0 dt_0}. \tag{291}$$

Let now the temperature be raised to t, while the body continues wholly liquid, but on the point of beginning to evaporate. This operation is indicated by DC.

The heat absorbed by the body during this change is $\int_{t_0}^{t} c_2 dt$, and the entropy changes from ϕ_1 to ϕ_2. Hence since $x = 0$, (273) gives by integration,

$$\phi_2 - \phi_1 = J \int_{t_0}^{t} c_2 e^{-\int \mu dt} dt. \tag{292}$$

Lastly, let the body expand isothermally till it reaches the state (x, t), indicated by B.

CB represents this change.

During this change the body absorbs λx or $\frac{1}{J}(\phi - \phi_2)\, e^{\int \mu dt}$ units of heat. Hence

$$\phi - \phi_2 = J\lambda x e^{-\int \mu dt}. \tag{293}$$

Summing these changes of entropy, we have

$$\begin{aligned} \phi - \phi_0 &= (\phi - \phi_2) + (\phi_2 - \phi_1) + (\phi_1 - \phi_0) \\ &= J\left[\lambda x e^{-\int \mu dt} + \int_{t_0}^{t} c_2 e^{-\int \mu dt} dt - \lambda_0 x_0 e^{-\int \mu_0 dt_0}\right], \end{aligned} \tag{294}$$

which is the same as (276).

To obtain the energy formula, let p_0 and p denote the pressures corresponding to the temperatures t_0 and t.

The increase of energy of the body during the compression AD will be

$$E_D - E_A = p_0(v_A - v_D) - J\lambda_0 x_0. \tag{295}$$

The energy acquired in the operation DC will be

$$E_C - E_D = \int_{v_D}^{v_C} p\, dv + J \int_{t_0}^{t} c_2 dt. \tag{296}$$

But v is nearly constant during this change, and consequently

$$\int_{v_D}^{v_C} p\,dv \doteq 0;$$

$$\therefore \quad E_C - E_D = J\int_{t_0}^{t} c_2\,dt. \qquad (297)$$

Lastly, the energy acquired in operation CB will be

$$E_B - E_C = J\lambda x - p\,(v_B - v_C). \qquad (298)$$

Summing these increments of energy, we get

$$E_B - E_A = (E_B - E_C) + (E_C - E_D) + (E_D - E_A)$$

$$= [J\lambda x - p\,(v_B - v_C)] + J\int_{t_0}^{t} c_2\,dt + [p_0\,(v_A - v_D) - J\lambda_0 x_0]$$

$$= J\,\{\lambda x - \lambda_0 x_0\} - p\,(v_B - v_C) + p_0(v_A - v_D) + J\int_{t_0}^{t} c_2\,dt.$$

Or since $v_C \doteq v_D \doteq V_2$ = a constant, (299)

$$E_B - E_A = J\,\{\lambda x - \lambda_0 x_0\} - (pv_B - p_0 v_A) + (p - p_0)\,V_2 + J\int_{t_0}^{t} c_2\,dt.$$

Or since c_2 is nearly constant, (300)

$$E_B - E_A = J\,(\lambda x - \lambda_0 x_0) - (pv_B - p_0 v_A) + (p - p_0)\,V_2 + Jc_2(t - t_0),$$

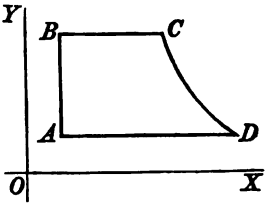
which is the same as (285). (301)

To illustrate what use may be made of these results, let us determine the work which would be done by a perfect heat engine working with steam and water through one or two cycles.

Taking first the following cycle:—

1st. Let unit mass of water, of temperature t_0, volume v_0, and pressure p_0, be heated in the cylinder to temperature t_1 and pressure p_1 without being allowed to expand.

Taking OX and OY as the axes of volume and pressure, let AB indicate this first change.



2nd. Let the contents of the cylinder expand at constant temperature t_1 and pressure p_1 till the volume and entropy become v_1 and ϕ_1.

Let BC denote this change.

3rd. Let the cylinder's contents expand further, adiabatically, till the temperature, pressure, and volume become t_0, p_0, and v_2.

Let CD denote this change.

4th. Let the contents of the cylinder now be compressed at constant temperature t_0, and pressure p_0, till its volume is reduced to v_0, its original value. This completes the cycle.

Let DA indicate this change.

In the first operation the cylinder's contents remain entirely liquid at or nearly at the point of beginning to evaporate, and absorb $c_2(t_1 - t_0)$ units of heat, while no external work is done.

In the second operation, if x_1 denote the quantity of water which evaporates, the cylinder's contents absorb $x_1\lambda_1$ units of heat, and perform $p_1(v_1 - v_0)$ units of external work.

In the third operation the contents of the cylinder receive no heat, and do external work of amount equal to $E_1 - E_2$, where E_1 and E_2 denote the intrinsic energy of the body in the states represented by C and D, that is, in the states at the beginning and end of the third operation.

In the fourth operation, heat of amount $x_0\lambda_0$ is emitted by the cylinder's contents, and external work of amount $p_0(v_2 - v_0)$ is expended in compressing it.

Here x_0 denotes the mass of steam at end of third operation.

Hence the total effective work obtained during the cycle is

$$W = p_1(v_1 - v_0) + (E_1 - E_2) - p_0(v_2 - v_0) \text{ or by } (285)$$

$$= p_1(v_1 - v_0) + \{J(\lambda_1 x_1 - \lambda_0 x_0) - (p_1 v_1 - p_0 v_2) + Jc_2(t_1 - t_0) + V_2(p_1 - p_0)\} - p_0(v_2 - v_0). \qquad (302)$$

Or, since v_0 is constant, and is approximately equal to V_2, this becomes

$$\left.\begin{aligned} W &= J(\lambda_1 x_1 - \lambda_0 x_0) + Jc_2(t_1 - t_0) \\ &= J\{(\lambda_1 x_1 - \lambda_0 x_0) + (t_1 - t_0)\}, \end{aligned}\right\} \qquad (303)$$

since $c_2 = 1$.

But by (279), since $\phi_C = \phi_D$,

$$\left.\begin{aligned} 0 &= \phi_C - \phi_D \\ &= J\left\{\frac{x_1\lambda_1}{\tau_1} - \frac{x_0\lambda_0}{\tau_0} + \log\frac{\tau_1}{\tau_0}\right\}; \\ \therefore\quad x_0\lambda_0 &= \tau_0\left\{\frac{x_1\lambda_1}{\tau_1} + \log\frac{\tau_1}{\tau_0}\right\}. \end{aligned}\right\} \qquad (304)$$

Hence (303) becomes

$$W = J\left\{\left[\frac{\lambda_1 x_1}{\tau_1} + 1\right](\tau_1 - \tau_0) - \tau_0 \log\frac{\tau_1}{\tau_0}\right\}. \qquad (305)$$

This is the same as Rankine's equation (1 A), § 284, "Steam Engine."

The result (303) may be more easily obtained thus:—

In any cycle

$$W = J\int dH,$$

where the integration extends over the cycle. Hence

$$W = J\left\{\int_0^{x_1}\left(\frac{dH}{dx}\right)_{t_1} dx + \int_{t_1}^{t_0}\left(\frac{dH}{dt}\right)_{\phi} dt + \int_{x_0}^{0}\left(\frac{dH}{dx}\right)_{t_0} dx + \int_{t_0}^{t_1}\left(\frac{dH}{dt}\right)_{v_0} dt\right\}$$

$$= J\{\lambda_1 x_1 + 0 - \lambda_0 x_0 + c_2(t_1 - t_0)\}$$

$$= J\{\lambda_1 x_1 - \lambda_0 x_0 + c_2(t_1 - t_0)\}.$$

If the adiabatic expansion of the third operation be allowed to go on till the temperature falls to $t_2 (> t_0)$, and if then the steam be suddenly admitted to the condenser, and the fourth operation or return stroke of the piston be performed under the pressure p_0 of the condenser, the work of the double stroke will be

$$\begin{aligned} W &= p_1(v_1 - v_0) + (E_1 - E_2) - p_0(v_2 - v_0) \\ &= p_1(v_1 - v_0) + \{[J(\lambda_1 x_1 + c_2 t_1) - p_1(v_1 - v_0)] \\ &\qquad - [J(\lambda_2 x_2 + c_2 t_2) - p_2(v_2 - v_0)]\} - p_0(v_2 - v_0) \\ &= J\{\lambda_1 x_1 - \lambda_2 x_2 + c_2(t_1 - t_2)\} + (p_2 - p_0)(v_2 - v_0). \quad (306) \end{aligned}$$

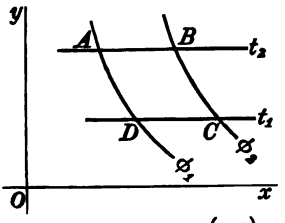
Or $$\begin{aligned} W &= J\int dH \\ &= J\lambda_1 x_1 + 0 + (E_0 - E_2) - J\lambda_0 x_0 + Jc_2(t_1 - t_0) \\ &= J\{\lambda_1 x_1 - \lambda_0 x_0 + c_2(t_1 - t_0)\} + \{[J(\lambda_0 x_0 + c_2 t_0) \\ &\qquad - p_0(v_2 - v_0)] - [J(\lambda_2 x_2 + c_2 t_2) - p_2(v_2 - v_0)]\} \\ &= J\{\lambda_1 x_1 - \lambda_2 x_2 + c_2(t_1 - t_2)\} + (p_2 - p_0)(v_2 - v_0). \end{aligned}$$

If the steam engine work with water and vapour through a finite isothermentropicycle, the work done is from (14) and (32),

$$\begin{aligned} W &= J\int dH \\ &= J\left\{\int_{\phi_1}^{\phi_2}\left(\frac{dH}{d\phi}\right)_{t_2} d\phi + \int_{t_2}^{t_1}\left(\frac{dH}{dt}\right)_{\phi_2} dt + \int_{\phi_2}^{\phi_1}\left(\frac{dH}{d\phi}\right)_{t_1} d\phi \right. \\ &\qquad \left. + \int_{t_1}^{t_2}\left(\frac{dH}{dt}\right)_{\phi_1} dt\right\} \\ &= \int_{\phi_1}^{\phi_2} e^{\int \mu_2 dt_2} d\phi + 0 + \int_{\phi_2}^{\phi_1} e^{\int \mu_1 dt_1} d\phi + 0 \\ &= e^{\int \mu_2 dt_2}(\phi_2 - \phi_1) + e^{\int \mu_1 dt_1}(\phi_1 - \phi_2) \end{aligned}$$

$$\left.\begin{aligned} &= (\phi_2 - \phi_1)\left[e^{\int \mu_2 dt_2} - e^{\int \mu_1 dt_1}\right] \\ &= (\phi_2 - \phi_1)(\tau_2 - \tau_1). \end{aligned}\right\} \qquad (307)$$

But if $\phi_1 = \phi_A$ and $\phi_2 = \phi_B$, then by (279), since t is constant,



$$\begin{aligned} \phi_2 - \phi_1 &= \phi_B - \phi_A \\ &= J\left(\frac{\lambda_2 x_B}{\tau_2} - \frac{\lambda_2 x_A}{\tau_2}\right) \\ &= J\left[\frac{\lambda_2(x_B - x_A)}{\tau_2}\right]. \end{aligned} \qquad (308)$$

Hence (307) becomes

$$W = J\lambda_2(x_B - x_A)\,\frac{\tau_2 - \tau_1}{\tau_2}. \qquad (309)$$

In the finite cycle represented by the isograph enclosed by the isograms (t_1, t_2, x_1, x_2), the external work done by a perfect engine will be

$$\begin{aligned} W &= J\int dH \\ &= J\left\{\int_{x_1}^{x_2}\left(\frac{dH}{dx}\right)_{t_2} dx + \int_{t_2}^{t_1}\left(\frac{dH}{dt}\right)_{x_2} dt + \int_{x_2}^{x_1}\left(\frac{dH}{dx}\right)_{t_1} dx \right. \\ &\qquad \left. + \int_{t_1}^{t_2}\left(\frac{dH}{dt}\right)_{x_1} dt\right\} \\ &= J\left\{\int_{x_1}^{x_2}\lambda_2\, dx + \int_{t_2}^{t_1}\left[c_1 x_2 + c_2(1 - x_2)\right] dt + \int_{x_2}^{x_1}\lambda_1\, dx \right. \\ &\qquad \left. + \int_{t_1}^{t_2}\left[c_1 x_1 + c_2(1 - x_1)\right] dt\right\} \\ &= J\left\{\lambda_2(x_2 - x_1) + x_2\int_{t_2}^{t_1} c_1\, dt + c_2(1 - x_2)(t_1 - t_2) + \lambda_1(x_1 - x_2) \right. \\ &\qquad \left. + x_1\int_{t_1}^{t_2} c_1\, dt + c_2(1 - x_1)(t_2 - t_1)\right\} \end{aligned}$$

$$= J\{(x_2 - x_1)(\lambda_2 - \lambda_1) + c_2(x_2 - x_1)(t_2 - t_1) - (x_2 - x_1)\int_{t_1}^{t_2} c_1\,dt\}$$

$$= J(x_2 - x_1)\{\lambda_2 - \lambda_1 + c_2(t_2 - t_1) - \int_{t_1}^{t_2} c_1\,dt\}$$

$$= J(x_2 - x_1)\int_{t_1}^{t_2}\left\{\frac{d\lambda}{dt} + (c_2 - c_1)\right\}dt$$

$$= J(x_2 - x_1)\int_{t_1}^{t_2}\lambda\mu\,dt \text{ from (253).}$$

Or, putting τ for t, and $\frac{1}{\tau}$ for μ,

$$W = J(x_2 - x_1)\int_{\tau_1}^{\tau_2}\frac{\lambda}{\tau}\,d\tau. \qquad (310)$$

If we suppose $x_1 = 0$, and $x_2 = 1$, this becomes

$$W = J\int_{\tau_1}^{\tau_2}\frac{\lambda}{\tau}\,d\tau. \qquad (311)$$

This gives the work which would be obtained by means of a perfect heat engine in the following cycle:—

1st. Starting with a pound of water in the cylinder at temperature τ_2, and about to begin to evaporate, let it evaporate at this temperature by allowing it to expand until it is all in the form of vapour, and at the same time it will take λ_2 units of heat from the source whose temperature is τ_2.

2nd. The dry saturated steam thus formed is now allowed to expand in such a way as to remain dry saturated steam until its temperature falls to τ_2. While this expansion is going on, $\int_{\tau_1}^{\tau_2} c_1\,d\tau$ units of heat will be given out by the steam.

3rd. The steam is now compressed at its present temperature, τ_1, until it all condenses into water. While this

operation is going on, the cylinder's contents will give out λ_1 units of heat to the refrigerator.

4th. The water is lastly raised from temperature τ_1 to temperature τ_2 by having c_2 units of heat given to it, while it remains constantly water in the state bordering on evaporation.

The pound of water has thus gone through a complete cycle of changes.

The algebraic sum of the quantities of heat it has received is

$$\int dH = \lambda_2 - \int_{\tau_1}^{\tau_2} c_1 d\tau - \lambda_1 + c_2(\tau_2 - \tau_1)$$

$$= (\lambda_2 - \lambda_1) + c_2(\tau_2 - \tau_1) - \int_{\tau_1}^{\tau_2} c_1 d\tau.$$

Hence the work of the cycle, which is the dynamical equivalent of this, must be

$$W = J \int dH$$

$$= J \left\{ (\lambda_2 - \lambda_1) + c_2(\tau_2 - \tau_1) - \int_{\tau_1}^{\tau_2} c_1 d\tau \right\}$$

$$= J \left\{ \int_{\tau_1}^{\tau_2} \left(\frac{d\lambda}{d\tau}\right) d\tau + \int_{\tau_1}^{\tau_2} c_2 d\tau - \int_{\tau_1}^{\tau_2} c_1 d\tau \right\}$$

$$= J \int_{\tau_1}^{\tau_2} \left\{ \left(\frac{d\lambda}{d\tau}\right) + (c_2 - c_1) \right\} d\tau$$

$$= J \int_{\tau_1}^{\tau_2} \frac{\lambda}{\tau} d\tau \text{ from (253).}$$

If the expansion along $x_2 = 1$ be stopped when $\tau = \tau' > \tau_1$, and the steam be then admitted to the condenser, and then

as before be compressed under pressure p_1, the pressure of the condenser, it is easily seen that the work will be

$$W = J\int_{\tau'}^{\tau_2}\frac{\lambda}{\tau}\,d\tau + (v' - v_0)(p' - p_1), \qquad (312)$$

where p' and v' are the volume and pressure immediately before admission to the condenser, and v_0 is the volume corresponding to state $x_1 = 0$, and is evidently equal to V_2, the volume of a pound of water in state $x_1 = 0$, which is practically constant.

Rankine has given the useful empirical formula connecting the pressure and volume of unit mass of dry saturated steam,

$$pv^{\frac{17}{16}} = \text{a constant}$$

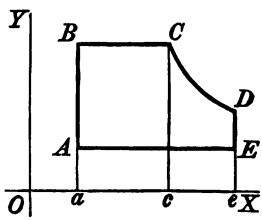
$$\doteq 475, \qquad (313)$$

where p denotes pounds per square inch, and v denotes cubic feet.

This relation must also hold for steam and water in the constant vapour-mass state denoted by

$$x = \text{a constant},$$

provided v refer to the portion in the state of vapour.



Let the accompanying diagram represent the cycle of which the work is expressed by (312).

Oa represents v_0 the volume of one pound of water just before evaporation begins at temperature τ_2.

Let BC represent the change in which the pound of water evaporates under pressure p_2 and temperature τ_2.

The work done during this expansion is represented by $BCcaB$, and expressed by

$$\begin{aligned} W_1 &= BCcaB \\ &= aB \,.\, ac \\ &= aB\,(Oc - Oa) \\ &= p_2\,(v_2 - v_0). \end{aligned} \tag{314}$$

Let CD represent the expansion of the pound of dry saturated steam from volume v_2 to v', while the temperature falls from τ_2 to τ'.

The work done during this expansion will, if we use (313), be

$$\begin{aligned} W_2 &= \int_{v_2}^{v'} p\,dv \\ &\doteqdot 475 \int_{v_2}^{v'} v^{-\frac{17}{16}} dv \\ &= 475\, \frac{v_2^{-\frac{1}{16}} - (v')^{-\frac{1}{16}}}{\frac{1}{16}} \\ &= 7600 \left[\frac{1}{v_2^{\frac{1}{16}}} - \frac{1}{(v')^{\frac{1}{16}}} \right]. \end{aligned} \tag{315}$$

Or, putting as Rankine does,

$$\left.\begin{aligned} \frac{v'}{v_2} &= r \\ \text{or} \qquad v' &= rv_2\,; \end{aligned}\right\} \tag{316}$$

and observing that from (313),

$$\frac{1}{v^{\frac{1}{16}}} = \frac{pv}{475}, \tag{317}$$

equation (315) becomes

$$\begin{aligned} W_2 &= 16\,(p_2 v_2 - p'v') \\ &= 16 p_2 v_2 [1 - r^{-\frac{1}{16}}]. \end{aligned} \tag{318}$$

Let DE represent the fall of pressure on admission of the steam to the condenser, and let EA represent the operation in which the steam is driven into the condenser by the return stroke of the piston.

The work used up in this operation is represented by $AEeaA$, and is expressed by

$$\begin{aligned} W_3 &= aA \,.\, ae \\ &= aA \,.\, (Oe - Oa) \\ &= p_1 (v' - v_0). \end{aligned} \tag{319}$$

Hence the total work of the double stroke will be

$$\begin{aligned} W &= W_1 + W_2 - W_3 \\ &= p_2(v_2 - v_0) + 16 p_2 v_2 [1 - r^{-\frac{1}{16}}] - p_1(v' - v_0)\,; \end{aligned} \tag{320}$$

or, since v_0 is very small, this is approximately

$$\begin{aligned} W &= p_2 v_2 + 16 p_2 v_2 [1 - r^{-\frac{1}{16}}] - p_1 v' \\ &= p_2 v_2 [17 - 16 r^{-\frac{1}{16}}] - p_1 v' \\ &= v' \{ p_2 (17 r^{-1} - 16 r^{-\frac{17}{16}}) - p_1 \}. \end{aligned} \tag{321}$$

This is formula (6), § 288, of Rankine's Treatise on the "Steam Engine."

Rankine's more accurate formula (3) of § 287 may easily be derived from (312) by substituting for λ its value given in (267). That is,

$$\begin{aligned} \lambda &= 607 - \cdot 708\, t \\ &= 607 - \cdot 708\, (\tau - 273) \\ &= 413 \cdot 7 - \cdot 708\, \tau\,; \end{aligned} \tag{322}$$

$$\therefore \quad \int_{\tau'}^{\tau_2} \frac{\lambda}{\tau}\, d\tau = 413 \cdot 7 \log \frac{\tau_2}{\tau'} - \cdot 708\, (\tau_2 - \tau'). \tag{323}$$

Therefore (312) becomes

$$W = 413{\cdot}7\, J \log \frac{\tau_2}{\tau'} - {\cdot}708\, J\,(\tau_2 - \tau') + (v' - v_0)\,(p' - p_1). \qquad (324)$$

Or, since $v_0 (= V_2)$, the volume of a pound of water, is very small, (324) becomes

$$W = 413{\cdot}7\, J \log \frac{\tau_2}{\tau_1} - {\cdot}708\, J\,(\tau_2 - \tau') + v'(p' - p_1), \qquad (325)$$

which is identical with Rankine's formula, except that this is adapted to the Centigrade scale, while Rankine's is adapted to the Fahrenheit scale.

It must, of course, be remarked that all these forms give the work done on *one* side of the piston in a *double* stroke.

The set of operations represented by *BCDEAB* is not, strictly speaking, a cycle, although it has inadvertently been called so here.

It is interesting to study the diagram of work for a mixture in which $V_2 > V_1$, that is, in which the lower form of the substance is less dense than the higher form, as in the case of a mixture of ice and water.

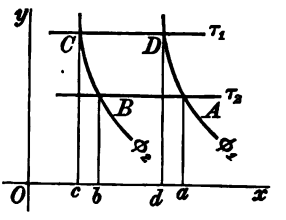
For the sake of being more definite, let us suppose the working body to be a mixture of water and ice, whose whole mass is one pound.

Starting with the body in the state represented by the point *A*, let the piston be pushed down, while the temperature is kept constant by having the conducting end of the cylinder in contact with the source whose temperature is τ_2. This *compression* will cause some of the ice to melt, and, as ice in melting absorbs heat, a quantity of heat is *taken in* by the body from the source.

This quantity may be expressed by either

$$\left.\begin{aligned} H_2 &= \frac{1}{J}\,\tau_2(\phi_2 - \phi_1), \\ \text{or by} \qquad H_2 &= \lambda_2(x_B - x_A), \end{aligned}\right\} \qquad (326)$$

where ϕ_1 and ϕ_2 denote the entropy of the body at the beginning and end of the operation, and x_A and x_B denote the mass of water in the mixture at the beginning and end of the operation.



Also work represented by $BAabB$ is expended in compressing the body.

The quantity of work so expended is expressed by

$$\begin{aligned} W_1 &= aA\,.\,ab \\ &= aA\,(Oa - Ob) \\ &= p_2(v_A - v_B). \end{aligned} \qquad (327)$$

Secondly, let the cylinder be placed on the non-conducting stand, and let the piston be pushed down through a distance represented by bc.

Let BC represent this operation.

During this compression more ice will melt, and, since the body is completely closed in with a non-conducting envelope, the temperature of the body will fall, owing to some of its sensible heat becoming latent by the melting of the ice.

Let the temperature fall to τ_1.

The work expended in this compression is represented by $BbcCB$, and expressed by

$$W_2 = \int_{v_C}^{v_B} p_{\phi_2}\,dv. \qquad (328)$$

No heat is taken in or given out during this operation.

Thirdly, let the cylinder be placed on the refrigerator, whose temperature is τ_1, and let the piston be allowed to rise until the entropy of the body falls to ϕ_1, its original value.

Let CD represent this operation.

During this expansion some of the water will become ice, and in doing so will cause some latent heat to become sensible. This heat will be given out to the refrigerator. Its value will be

$$\left.\begin{aligned} H_1 &= \frac{1}{J}\tau_1(\phi_2 - \phi_1), \\ \text{or} \qquad H_1 &= \lambda_1(x_C - x_D), \end{aligned}\right\} \tag{329}$$

where ϕ_1 and ϕ_2 denote the entropy of the body, and x_C and x_D the mass of water at the beginning and end of this operation.

And the work done during this operation is represented by $CDdcC$, and expressed by

$$\begin{aligned} W_3 &= cC \,.\, cd \\ &= cC\,(Od - Oc) \\ &= p_1(v_D - v_C). \end{aligned} \tag{330}$$

Fourthly, let the cylinder be placed on the non-conducting stand, and let the piston rise until the volume of the body returns to its original value. Its volume and entropy being the same as at first, its temperature will be τ_2, what it was at first.

Let DA represent this operation.

No heat is taken in or given out by the body during this operation, but work is done by it in expanding, represented by $DAadD$, and expressed by

$$W_4 = \int_{v_D}^{v_A} p_{\phi_1} dv. \tag{331}$$

The excess of the external work done by the body in expanding during the cycle over the work done in compressing it is represented by $ABCDA$, and is expressed by

$$W = (W_3 + W_4) - (W_1 + W_2)$$
$$= \left[p_1(v_D - v_C) + \int_{v_D}^{v_A} p_{\phi_1} dv\right] - \left[p_2(v_A - v_B) + \int_{v_C}^{v_B} p_{\phi_2} dv\right]. \quad (332)$$

And the excess of the heat taken in over the heat given out by the body during the cycle will be

$$\left.\begin{aligned} H &= H_2 - H_1 \\ &= \lambda_2(x_B - x_A) - \lambda_1(x_C - x_D), \\ \text{or} \quad H &= H_2 - H_1 \\ &= \frac{1}{J}\left[\tau_2(\phi_2 - \phi_1) - \tau_1(\phi_2 - \phi_1)\right] \\ &= \frac{1}{J}(\tau_2 - \tau_1)(\phi_2 - \phi_1). \end{aligned}\right\} \quad (333)$$

And since $W = J \,.\, H$, we have

$$W = (\tau_2 - \tau_1)(\phi_2 - \phi_1), \quad (334)$$

which is the same as (307), or

$$W = J\{\lambda_2(x_B - x_A) - \lambda_1(x_C - x_D)\}. \quad (335)$$

But from (280),

$$\frac{J\lambda_1(x_C - x_D)}{\tau_1} = \phi_2 - \phi_1 = \frac{J\lambda_2(x_B - x_A)}{\tau_2}. \quad (336)$$

Hence by substitution from this (335) becomes

$$W = J\lambda_2(x_B - x_A)\left\{1 - \frac{\tau_1}{\tau_2}\right\}$$
$$= J\lambda_2(x_B - x_A)\frac{\tau_2 - \tau_1}{\tau_2}, \quad (337)$$

which is the same as (309).

That the isothermal τ_2 is below the isothermal τ_1, or that the isothermal of the higher temperature corresponds to the lower pressure follows from (260), which shows that for a mixture of two portions of the same substance in different states,

$$\frac{d\tau}{dp} = \text{a negative quantity,}$$

if $$V_1 < V_2;$$

i.e. if the volume of unit mass of the higher form is less than the volume of unit mass of the lower form, and that therefore the temperature falls when the pressure is increased, and the temperature rises when the pressure is diminished.

Again, that the higher isentrope ϕ_2 corresponds to the smaller volume, as in the figure, follows from (280) and (254).

For from (280),

$$\left.\begin{aligned}\left(\frac{d\phi}{dv}\right)_\tau &= \frac{J\lambda}{\tau}\left(\frac{dx}{dv}\right)_\tau \\ &= \frac{J\lambda}{\tau}\cdot\frac{1}{V_1 - V_2} \text{ from (254)} \\ &= \text{a negative quantity,}\end{aligned}\right\} \quad (338)$$

since $$V_1 < V_2.$$

Hence, as v increases isothermally, ϕ diminishes.

CHAPTER XV.

USUAL METHOD OF OBTAINING THERMODYNAMIC FORMULÆ.

HAVING shown in the foregoing Chapters how all thermodynamic formulæ spring naturally from definitions, experimental results, and the Two Laws as expressed in (24) and (39), I shall in this Chapter indicate shortly the usual mode of deriving many of these formulæ.

This method, though very admirable, labours under the disadvantage of causing the formulæ to appear bound together by *mathematical* rather than by *physical laws*.

Starting with the self-evident equation

$$dH = M dv + N dt, \tag{339}$$

which asserts that, of the heat dH added to a body, the part $M dv$ would increase its volume by dv, while its temperature is maintained constant by varying the pressure, and the other portion $N dt$ would increase its temperature by dt, while its volume is kept constant.

The part $N dt$ does not contribute to the quantity of *external* work done by the body, but only affects its temperature, and possibly does *internal* work among the molecules of the body which is stored up in potential form among the molecules.

Of the portion $M dv$ a part is used up in doing external work of amount $p dv$ in overcoming external pressure, while the body is expanding by the amount dv.

The expression for this quantity will be $\frac{p\,dv}{J}$.

The remainder $M\,dv - \frac{p\,dv}{J}$ will go to perform the internal work necessary to cause the body to expand by dv.

If E be put for the whole energy of the body, including sensible heat and potential molecular energy, and if dE denote the increase of this due to the addition of dH units of heat, dE will be the dynamical equivalent of the quantity of heat,

$$\left(M - \frac{p}{J}\right) dv + N\,dt.$$

Hence

$$dE = J\left\{\left(M - \frac{p}{J}\right) dv + N\,dt\right\}$$

$$= (JM - p)\,dv + JN\,dt. \qquad (340)$$

Now it is axiomatic that the internal energy of a body will always be the same for the same state of the body as regards volume and temperature. Hence E must be a function of v and t, and therefore from (340) it follows that

$$\left(\frac{dE}{dv}\right)_t = JM - p, \qquad (341)$$

and

$$\left(\frac{dE}{dt}\right)_v = JN. \qquad (342)$$

But by the principles of the differential calculus,

$$\left(\frac{d}{dt}\right)_v \left(\frac{dE}{dv}\right)_t = \left(\frac{d}{dv}\right)_t \left(\frac{dE}{dt}\right)_v, \qquad (343)$$

which from (341) and (342) becomes

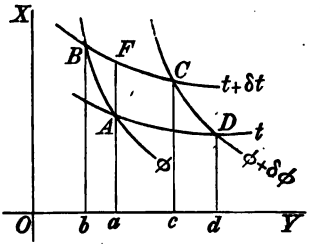
$$\left(\frac{d}{dt}\right)_v [JM - p] = \left(\frac{d}{dv}\right)_t \left(JN\right),$$

or

$$J\left(\frac{dM}{dt}\right)_v - \left(\frac{dp}{dt}\right)_v = J\left(\frac{dN}{dv}\right)_t,$$

or
$$J\left\{\left(\frac{dM}{dt}\right)_v - \left(\frac{dN}{dv}\right)_t\right\} = \left(\frac{dp}{dt}\right)_v, \tag{344}$$

which is the same as (45), one of the expressions we obtained of the First Law.



The Second Law is proved much as we have already proved it.

Let $ABCD$ represent Carnot's cycle as amended by Clerk Maxwell.

Then

$$\mu = \frac{\text{work of cycle}}{\text{heat received from source} \times \text{range} \times J}$$

$$= \frac{\text{area of } ABCD}{M\,dv \times \delta t \times J}$$

$$= \frac{ad \times AF}{M\,.\,bc \times \delta t \times J}$$

$$= \frac{AF}{JM\,\delta t} \quad \because\ bc = ad$$

$$= \frac{\left(\frac{dp}{dt}\right)_v . \delta t}{JM\,\delta t} = \frac{\left(\frac{dp}{dt}\right)_v}{JM}. \tag{345}$$

From this and (344),

$$\left.\begin{aligned} &\left(\frac{dM}{dt}\right)_v - \left(\frac{dN}{dv}\right)_t = M\mu, \\ \text{or}\quad &\left(\frac{dM}{d\tau}\right)_v - \left(\frac{dN}{dv}\right)_\tau = \frac{M}{\tau}. \end{aligned}\right\} \tag{346}$$

From this it follows that

$$\left(\frac{dM}{d\tau}\right)_v \text{ is not equal to } \left(\frac{dN}{dv}\right)_\tau;$$

and therefore from this and (339) it follows that dH is not a complete differential of the two independent variables v and t.

This is otherwise evident: because, if H denote the quantity of heat the body receives in passing from some standard state to any other state, H will depend not only on the new state, but on the series of changes by which the body passes from the one state to the other, because a portion of H is used up in external work; and although the portion of H which is not thus used up is the same for every series of changes, the part used up in external work is not.

But, although dH is not a complete differential of the variables v and t, it can be made so by the multiplier $e^{-\int \mu dt}$.

For if we multiply (339) by $e^{-\int \mu dt}$, it becomes

$$e^{-\int \mu dt} dH = e^{-\int \mu dt} . M dv + e^{-\int \mu dt} N dt. \tag{347}$$

Now
$$\left(\frac{d}{dt}\right)_v \left[Me^{-\int \mu dt}\right] - \left(\frac{d}{dv}\right)_t \left[Ne^{-\int \mu dt}\right]$$
$$= \left(\frac{dM}{dt}\right)_v e^{-\int \mu dt} - M\mu e^{-\int \mu dt} - \left(\frac{dN}{dv}\right)_t e^{-\int \mu dt}$$
$$= \left\{\left(\frac{dM}{dt}\right)_v - \left(\frac{dN}{dv}\right)_t - M\mu\right\} e^{-\int \mu dt}. \tag{348}$$

But by (346),
$$\left(\frac{dM}{dt}\right)_v - \left(\frac{dN}{dv}\right)_t - M\mu = 0. \tag{349}$$

Hence (348) becomes
$$\left.\begin{aligned} &\left(\frac{d}{dt}\right)_v \left[Me^{-\int \mu dt}\right] - \left(\frac{d}{dv}\right)_t \left[Ne^{-\int \mu dt}\right] = 0, \\ \text{or} \quad &\left(\frac{d}{dt}\right)_v \left[Me^{-\int \mu dt}\right] = \left(\frac{d}{dv}\right)_t \left[Ne^{-\int \mu dt}\right]. \end{aligned}\right\} \tag{350}$$

Hence from this and (347), $e^{-\int \mu dt} dH$ is a complete differential of some function of the independent variables v and t.

But returning to the fundamental equation (18) derived from Carnot's cycle,

$$\mu = \frac{1}{h}\left(\frac{dh}{dt}\right), \tag{351}$$

where h, besides being a function of t, is a function of the two isentropic states denoted by ϕ and $\phi + \delta\phi$.

Hence the integral of (351) must be of the form

$$h = \Phi e^{\int \mu dt}, \tag{352}$$

where Φ is a function of ϕ and $\phi + \delta\phi$.

Choosing our system of adiabatics, which may be chosen arbitrarily, so as to give the simplest possible form to this equation. Let

$$\begin{aligned} \Phi &= (\phi + \delta\phi) - \phi \\ &= \delta\phi. \end{aligned} \tag{353}$$

Hence equation (352) becomes

$$h = \delta\phi \,.\, e^{\int \mu dt}. \tag{354}$$

or putting $\left(\frac{dH}{d\phi}\right)_t \delta\phi$ for h,

$$\left(\frac{dH}{d\phi}\right)_t = e^{\int \mu dt}. \tag{355}$$

And since

$$\left(\frac{dH}{dt}\right)_\phi = 0; \tag{356}$$

$$\left.\begin{aligned} \therefore \quad \delta H &= \left(\frac{dH}{d\phi}\right)_t \delta\phi + \left(\frac{dH}{dt}\right)_\phi dt \\ &= e^{\int \mu dt} d\phi; \end{aligned}\right\} \tag{357}$$

$$\left.\begin{aligned} \therefore \quad \delta\phi &= e^{-\int \mu dt} \delta H \\ &= e^{-\int \mu dt} M dv + e^{-\int \mu dt} N dt. \end{aligned}\right\} \tag{358}$$

Hence since $\delta\phi$ or $e^{-\int\mu dt}\delta H$ is a complete differential of the variables v and t,

$$\left(\frac{d\phi}{dv}\right)_t = Me^{-\int\mu dt}, \tag{359}$$

and

$$\left(\frac{d\phi}{dt}\right)_v = Ne^{-\int\mu dt}; \tag{360}$$

or, if we put $t = \tau$, and $\mu = \frac{1}{\tau}$,

$$\left(\frac{d\phi}{dv}\right)_\tau = \frac{M}{\tau}, \tag{361}$$

and

$$\left(\frac{d\phi}{d\tau}\right)_v = \frac{N}{\tau}. \tag{362}$$

And (357) becomes

$$\delta H = \tau\delta\phi. \tag{363}$$

This work of course becomes simpler if we confine it to the absolute scale as defined by Thomson.

Thus by his definition,

$$\frac{h + \delta h}{\tau + \delta\tau} = \frac{h}{\tau} = \text{a constant between the same isentropes.}$$

Hence $\frac{h}{\tau}$ must be a function $\phi + \delta\phi$ and ϕ. And since the numbering of the isentropes is arbitrary, we may number them so as to make this function the simplest possible.

That is, we may put

$$\frac{h + \delta h}{\tau + \delta\tau} = \frac{h}{\tau} = (\phi + \delta\phi) - \phi = \delta\phi; \tag{364}$$

$$\therefore \quad h = \tau\,\delta\phi;$$

or, putting δH for h,

$$\delta H = \tau\,\delta\phi. \tag{365}$$

By (340),

$$\begin{aligned}\delta E &= J\delta H - p\delta v \\ &= Je^{\int\mu dt}\delta\phi - p\,.\,\delta v. \end{aligned} \tag{366}$$

This must be a complete differential, because if any two of p, v, t, ϕ, E are known, the others follow.

Hence from (366) we see that

$$\left(\frac{dE}{d\phi}\right)_v = Je^{\int \mu dt} = J\tau, \tag{367}$$

and

$$\left(\frac{dE}{dv}\right)_\phi = -p. \tag{368}$$

But by the principles of the Differential Calculus,

$$\left(\frac{d}{dv}\right)_\phi \left(\frac{dE}{d\phi}\right)_v = \left(\frac{d}{d\phi}\right)_v \left(\frac{dE}{dv}\right)_\phi.$$

Hence

$$\left(\frac{d}{dv}\right)_\phi \left[Je^{\int \mu dt}\right] = \left(\frac{d}{d\phi}\right)_v [-p],$$

or

$$\left(\frac{dt}{dv}\right)_\phi \left(\frac{d}{dt}\right)_\phi \left[Je^{\int \mu dt}\right] = -\left(\frac{dp}{d\phi}\right)_v,$$

or

$$J\mu e^{\int \mu dt}\left(\frac{dt}{dv}\right)_\phi = -\left(\frac{dp}{d\phi}\right)_v;$$

and therefore

$$J\left(\frac{d\tau}{dv}\right)_\phi = -\left(\frac{dp}{d\phi}\right)_v. \tag{369}$$

Any combination of p, v, t, ϕ, E will be a function of any two of these.

Hence $A.E + B.pv + C.Je^{\int \mu dt}\phi$ will be a function of any two of p, v, t, ϕ, E, if A, B, and C be any constants.

Hence by giving A, B, and C various values, we can get a variety of results thus:—

$$\begin{aligned}\delta\left[AE + Bpv + CJe^{\int \mu dt}\phi\right] &= A\delta E + B\delta(pv) + CJ\delta\left(e^{\int \mu dt}\phi\right)\\ &= A\left[Je^{\int \mu dt}\delta\phi - p\delta v\right] + B\left[p\delta v + v\delta p\right]\\ &\qquad + CJe^{\int \mu dt}\left[\delta\phi + \phi\mu\delta t\right]\\ &= (A + C)\,Je^{\int \mu dt}\delta\phi - (A - B)\,p\delta v\\ &\qquad + Bv\delta p + CJ\mu\phi e^{\int \mu dt}\delta t. \end{aligned} \tag{370}$$

If we put $A = B = 1$, and $C = 0$, this becomes

$$\left.\begin{aligned}\delta[E + pv] &= Je^{\int\mu dt}\,\delta\phi + v\delta p\\ &= J\tau\delta\phi + v\delta p.\end{aligned}\right\} \tag{371}$$

And since this is a complete differential of ϕ and p,

$$\left.\begin{aligned}\left(\frac{d}{d\phi}\right)_p[E + pv] &= Je^{\int\mu dt},\\ \text{or}\qquad &= J\tau,\end{aligned}\right\} \tag{372}$$

and
$$\left(\frac{d}{dp}\right)_\phi[E + pv] = v\,; \tag{373}$$

and therefore

$$\left(\frac{d}{dp}\right)_\phi\left[Je^{\int\mu dt}\right] = \left(\frac{d}{d\phi}\right)_p(v),$$

$$\left.\begin{aligned}\text{or}\qquad J\mu e^{\int\mu dt}\left(\frac{dt}{dp}\right)_\phi &= \left(\frac{dv}{d\phi}\right)_p,\\ \text{or}\qquad J\left(\frac{d\tau}{dp}\right)_\phi &= \left(\frac{dv}{d\phi}\right)_p.\end{aligned}\right\} \tag{374}$$

Again if in (370) we put

$$A = -C = 1, \text{ and } B = 0,$$

$$\left.\begin{aligned}\text{we get}\qquad \delta[E - Je^{\int\mu dt}\phi] &= -p\delta v - J\mu\phi e^{\int\mu dt}\delta t,\\ \text{or}\qquad \delta[E - J\tau\phi] &= -p\delta v - J\phi\delta\tau,\end{aligned}\right\} \tag{375}$$

which must be a complete differential. Hence

$$\left.\begin{aligned}\left(\frac{d}{dv}\right)_t[E - J\phi e^{\int\mu dt}] &= -p,\\ \text{or}\qquad \left(\frac{d}{dv}\right)_\tau[E - J\phi\tau] &= -p\,;\end{aligned}\right\} \tag{376}$$

$$\left.\begin{aligned}\text{and}\qquad \left(\frac{d}{dt}\right)_v[E - J\phi e^{\int\mu dt}] &= -J\phi\mu e^{\int\mu dt},\\ \text{or}\qquad \left(\frac{d}{d\tau}\right)_v[E - J\phi\tau] &= -J\phi.\end{aligned}\right\} \tag{377}$$

And therefore

$$\left(\frac{d}{dt}\right)_v [-p] = \left(\frac{d}{dv}\right)_t [-J\mu\phi e^{\int \mu dt}],$$

$$\left.\begin{aligned} &i.e. \quad \left(\frac{dp}{dt}\right)_v = J\left(\frac{d\phi}{dv}\right)_t \mu e^{\int \mu dt}, \\ &\text{or} \quad \left(\frac{dp}{d\tau}\right)_v = J\left(\frac{d\phi}{dv}\right)_\tau. \end{aligned}\right\} \quad (378)$$

Again, if in (370) we put

$$A = B = -C = 1,$$

$$\left.\begin{aligned} &\text{we get} \quad \delta[E + pv - Je^{\int \mu dt}\phi] = v\delta p - J\mu\phi e^{\int \mu dt}\delta t, \\ &\text{or} \quad \delta[E + pv - J\tau\phi] \quad = v\delta p - J\phi\delta\tau. \end{aligned}\right\} \quad (379)$$

And since this is a complete differential,

$$\left.\begin{aligned} &\left(\frac{d}{dp}\right)_t [E + pv - Je^{\int \mu dt}\phi] = v, \\ &\text{or} \quad \left(\frac{d}{dp}\right)_\tau [E + pv - J\tau\phi] = v; \end{aligned}\right\} \quad (380)$$

$$\left.\begin{aligned} &\text{and} \quad \left(\frac{d}{dt}\right)_p [E + pv - Je^{\int \mu dt}\phi] = -J\mu\phi e^{\int \mu dt}, \\ &\text{or} \quad \left(\frac{d}{d\tau}\right)_p [E + pv - J\tau\phi] = -J\phi. \end{aligned}\right\} \quad (381)$$

And therefore by the Differential Calculus,

$$\left(\frac{d}{dt}\right)_p (v) = \left(\frac{d}{dp}\right)_t [-J\phi\mu e^{\int \mu dt}],$$

$$\left.\begin{aligned} &i.e. \quad \left(\frac{dv}{dt}\right)_p \quad = -J\mu e^{\int \mu dt}\left(\frac{d\phi}{dp}\right)_t, \\ &\text{or} \quad \left(\frac{dv}{d\tau}\right)_p \quad = -J\left(\frac{d\phi}{dp}\right)_\tau. \end{aligned}\right\} \quad (382)$$

If the pressure of the working substance be kept constant,

$$K\delta t = \delta H$$

$$= M\delta v + N\delta t;$$

$$\therefore \quad K = M\left(\frac{dv}{dt}\right)_p + N; \tag{383}$$

$$\therefore \quad \left(\frac{dv}{dt}\right)_p = \frac{K - N}{M}. \tag{384}$$

Again,

$$e^{\int \mu dt}\delta\phi = \delta H$$

$$= M\delta v + N\delta t.$$

Hence, if ϕ be constant, and $\therefore \delta\phi = 0$, this becomes

$$0 = M\delta v + N\delta t;$$

$$\therefore \quad \left(\frac{dv}{dt}\right)_\phi = -\frac{N}{M}, \tag{385}$$

which is the differential equation of an adiabatic or isentrope.

Again,

$$e^{\int \mu dt}\delta\phi = \delta H$$

$$= \left(\frac{dH}{dp}\right)_t \delta p + \left(\frac{dH}{dt}\right)_p \delta t$$

$$= \left(\frac{dH}{dv}\right)_t \left(\frac{dv}{dp}\right)_t \delta p + \left(\frac{dH}{dt}\right)_p \delta t$$

$$= M\left(\frac{dv}{dp}\right)_t \delta p + K\delta t. \tag{386}$$

Hence, if ϕ is constant, this becomes

$$0 = M\left(\frac{dv}{dp}\right)_t \delta p + K\delta t;$$

$$\therefore \quad M\left(\frac{dv}{dp}\right)_t \left(\frac{dp}{dt}\right)_\phi + K = 0. \tag{387}$$

Again,
$$e^{\int \mu dt}\delta\phi = M\delta v + N\delta t$$
$$= M\delta v + N\left\{\left(\frac{dt}{dv}\right)_p \delta v + \left(\frac{dt}{dp}\right)_v \delta p\right\}$$
$$= \left[M + N\left(\frac{dt}{dv}\right)_p\right]\delta v + N\left(\frac{dt}{dp}\right)_v \delta p$$
$$= K\left(\frac{dt}{dv}\right)_p \delta v + N\left(\frac{dt}{dp}\right)_v \delta p. \qquad (388)$$

Or thus,
$$e^{\int \mu dt}\delta\phi = \delta H$$
$$= \left(\frac{dH}{dv}\right)_p \delta v + \left(\frac{dH}{dp}\right)_v \delta p$$
$$= \left(\frac{dH}{dt}\right)_p \cdot \left(\frac{dt}{dv}\right)_p \delta v + \left(\frac{dH}{dt}\right)_v \left(\frac{dt}{dp}\right)_v \delta p$$
$$= K\left(\frac{dt}{dv}\right)_p \delta v + N\left(\frac{dt}{dp}\right)_v \delta p. \qquad (388)$$

Hence, if ϕ is constant,
$$K\left(\frac{dt}{dv}\right)_p \delta v + N\left(\frac{dt}{dp}\right)_v \delta p = 0,$$
or
$$K\left(\frac{dt}{dv}\right)_p + N\left(\frac{dt}{dp}\right)_v \left(\frac{dp}{dv}\right)_\phi = 0. \qquad (389)$$

Also, since ϕ is a function of v and p, we have from (388),
$$\left(\frac{d\phi}{dv}\right)_p = Ke^{-\int \mu dt}\left(\frac{dt}{dv}\right)_p, \qquad (390)$$
and
$$\left(\frac{d\phi}{dp}\right)_v = Ne^{-\int \mu dt}\left(\frac{dt}{dp}\right)_v. \qquad (391)$$

And therefore by the Differential Calculus,
$$\left.\begin{aligned} &\left(\frac{d}{dp}\right)_v \left[Ke^{-\int \mu dt}\left(\frac{dt}{dv}\right)_p\right] = \left(\frac{d}{dv}\right)_p \left[Ne^{-\int \mu dt}\left(\frac{dt}{dp}\right)_v\right], \\ \text{or}\quad &\left(\frac{d}{dp}\right)_v \left[\frac{K}{\tau}\left(\frac{d\tau}{dv}\right)_p\right] = \left(\frac{d}{dv}\right)_p \left[\frac{N}{\tau}\left(\frac{d\tau}{dp}\right)_v\right]. \end{aligned}\right\} \qquad (392)$$

Similarly from (386) we have

$$\left.\begin{aligned} &\left(\frac{d}{dt}\right)_p\left[Me^{-\int\mu dt}\left(\frac{dv}{dp}\right)_t\right]=\left(\frac{d}{dp}\right)_t\left[Ke^{-\int\mu dt}\right], \\ \text{or}\quad &\left(\frac{d}{d\tau}\right)_p\left[\frac{M}{\tau}\left(\frac{dv}{dp}\right)_\tau\right]=\left(\frac{d}{dp}\right)_\tau\left[\frac{K}{\tau}\right]. \end{aligned}\right\} \tag{393}$$

Many other results may be obtained in a similar way.

We shall take one more example. For the case of a body consisting of masses x and $1-x$ of a substance in a higher and lower form, having c_1 and c_2 for their specific heats, and having λ for the latent heat of unit mass of the higher form,

$$\begin{aligned} e^{\int\mu dt}\,\delta\phi &= \delta H \\ &= \lambda\delta x+\left[c_1x+(1-x)\,c_2\right]\delta t. \end{aligned} \tag{394}$$

That is, if δH units of heat be added to the body, the quantity $\lambda\delta x$ goes to convert the mass δx from the lower to the higher form, and $\left[c_1x+(1-x)\,c_2\right]\delta t$ goes to raise the temperature of the whole by δt.

Hence, since ϕ is a function of x and t,

$$\left.\begin{aligned} &\left(\frac{d\phi}{dx}\right)_t=\lambda e^{-\int\mu dt}, \\ \text{or}\quad &\left(\frac{d\phi}{dx}\right)_\tau=\frac{\lambda}{\tau}; \end{aligned}\right\} \tag{395}$$

and

$$\left.\begin{aligned} &\left(\frac{d\phi}{dt}\right)_x=\left[c_1x+c_2(1-x)\right]e^{-\int\mu dt}, \\ \text{or}\quad &\left(\frac{d\phi}{d\tau}\right)_x=\frac{c_1x+c_2(1-x)}{\tau}. \end{aligned}\right\} \tag{396}$$

Hence by the Differential Calculus,

$$\left.\begin{aligned} &\left(\frac{d}{dt}\right)_x\left(\lambda e^{-\int\mu dt}\right)=\left(\frac{d}{dx}\right)_t\left\{\left[c_1x+c_2(1-x)\right]e^{-\int\mu dt}\right\}, \\ \text{or}\quad &\left(\frac{d}{d\tau}\right)_x\left(\frac{\lambda}{\tau}\right)=\left(\frac{d}{dx}\right)_\tau\left(\frac{c_1x+c_2(1-x)}{\tau}\right). \end{aligned}\right\} \tag{397}$$

Performing these differentiations, we get

$$\left.\begin{aligned} &\left(\frac{d\lambda}{dt}\right)_x - \mu\lambda = c_1 - c_2, \\ \text{or}\quad &\left(\frac{d\lambda}{d\tau}\right)_x - \frac{\lambda}{\tau} = c_1 - c_2. \end{aligned}\right\} \tag{398}$$

Or since λ is a function of t only, these may be written

$$\left.\begin{aligned} &\frac{d\lambda}{dt} - \mu\lambda = c_1 - c_2, \\ \text{or}\quad &\frac{d\lambda}{d\tau} - \frac{\lambda}{\tau} = c_1 - c_2. \end{aligned}\right\} \tag{399}$$

If the body be compressed adiabatically,

$$\delta\phi = 0.$$

Hence (394) becomes

$$0 = \lambda\delta x + [c_1 x + c_2(1-x)]\,\delta t;$$

$$\therefore\quad \left(\frac{dx}{dt}\right)_\phi = -\frac{c_1 x + c_2(1-x)}{\lambda}. \tag{400}$$

Hence from this and (258),

$$\left.\begin{aligned} \left(\frac{dx}{dp}\right)_\phi &= \left(\frac{dx}{dt}\right)_\phi \cdot \left(\frac{dt}{dp}\right)_\phi \\ &= -\frac{c_1 x + c_2(1-x)}{\lambda} \cdot \frac{V_1 - V_2}{J\lambda\mu} \\ &= -\frac{[c_1 x + c_2(1-x)](V_1 - V_2)}{J\lambda^2\mu}, \\ \text{or}\quad &\quad -\frac{[c_1 x + c_2(1-x)](V_1 - V_2)\tau}{J\lambda^2}. \end{aligned}\right\} \tag{401}$$

Hence if $V_1 > V_2$, as in the case of a body consisting of a vapour and its liquid in contact, or of solid and liquid sulphur,

$$\left(\frac{dx}{dp}\right)_\phi = \left\{\begin{array}{l} \text{a negative quantity,} \\ \text{zero, or} \\ \text{a positive quantity,} \end{array}\right.$$

according as

$$c_1 x + c_2(1 - x) = \begin{cases} \text{a positive quantity,} \\ \text{zero, or} \\ \text{a negative quantity;} \end{cases}$$

that is, according as

$$x \lessgtr \frac{c_2}{c_2 - c_1},$$

if $c_2 > c_1$.

Now since x cannot be greater than unity, and

$$\frac{c_2}{c_2 - c_1} > 1,$$

if c_1 and c_2 are both positive, and $c_2 > c_1$ in such a case we can have nothing else than

$$x < \frac{c_2}{c_2 - c_1};$$

and $\therefore \left(\frac{dx}{dp}\right)_\phi =$ a negative quantity.

Hence for such a body compression will cause the quantity of the higher form to diminish, that is, will cause condensation in the case of a vapour and its liquid, and will cause solidification in the case of a body consisting of a mixture of the solid and liquid forms of the same substance.

If for a body consisting of a liquid and its vapour,

$$c_1 = \text{a negative quantity,}$$

and $\therefore \quad c_2 > c_1,$

as is the case for water, bisulphide of carbon, bichloride of carbon, chloroform, and aceton,

and $\therefore \quad \frac{c_2}{c_2 - c_1} < 1$

compression will cause *condensation* if

$$x < \frac{c_2}{c_2 - c_1};$$

evaporation, if
$$x > \frac{c_2}{c_2 - c_1},$$
and *neither*, if
$$x = \frac{c_2}{c_2 - c_1}.$$

If, as in the case of ice and water, $c_1 > c_2$, and both are positive, and $\therefore\ c_1 x + c_2(1 - x) =$ a positive quantity, whatever be the value of x (of course x cannot be greater than 1) for such a body,

$$\left(\frac{dx}{dp}\right)_\phi = \begin{cases} \text{a negative quantity, or} \\ \text{a positive quantity,} \end{cases}$$

according as
$$V_1 \gtrless V_2.$$

In the case of *ice and water*,
$$V_1 < V_2;$$
$$\therefore\ \left(\frac{dx}{dp}\right)_\phi = \text{a positive quantity.}$$

Hence *compression causes liquefaction.*

In the case of *solid and liquid sulphur*,
$$V_1 > V_2.$$

Hence
$$\left(\frac{dx}{dp}\right)_\phi = \text{a negative quantity.}$$

Therefore *compression will cause solidification.*

From (387),
$$\left(\frac{dt}{dp}\right)_\phi = -\frac{M\left(\frac{dv}{dp}\right)_t}{K}$$
$$= -\frac{\left(\frac{dp}{dt}\right)_v \cdot \left(\frac{dv}{dp}\right)_t}{JK\mu} \text{ by (345)}$$

$$= -\frac{1}{JK\mu} \cdot \frac{\left(\frac{dp}{dt}\right)_v}{\left(\frac{dp}{dv}\right)_t}$$

$$= \frac{1}{JK\mu}\left(\frac{dv}{dt}\right)_p \text{ by (1)}$$

$$= \frac{ev}{JK\mu} \text{ by (99)}$$

$$= \frac{e(v\rho)}{J(K\rho)\mu}$$

$$= \frac{eW}{JS\mu}. \qquad (402)$$

Hence for sudden (or adiabatic) compression,

$$\delta t = \frac{eW}{J\mu S} \cdot \delta p, \qquad (403)$$

where W = the mass of the body;

and $S = K\rho$ = the capacity for heat of unit volume under constant pressure.

From (383),

$$K - N = M\left(\frac{dv}{dt}\right)_p$$

$$= \frac{1}{J\mu}\left(\frac{dp}{dt}\right)_v \cdot \left(\frac{dv}{dt}\right)_p \text{ by (345)}$$

$$= \frac{1}{J\mu} \cdot (ke) \cdot (ev) \text{ by (99) and (100)}$$

$$= \frac{ke^2 v}{J\mu}. \qquad (404)$$

The equation for a gas is

$$pv = p_0 v_0 (1 + Et), \qquad (405)$$

where t is temperature counted from 0° C.;

$$\therefore \left(\frac{dp}{dt}\right)_v = \frac{p_0 v_0 E}{v}. \qquad (406)$$

But from (345),

$$\mu = \frac{1}{JM}\left(\frac{dp}{dt}\right)_v$$

$$= \frac{1}{JM} \cdot \frac{p_0 v_0 E}{v} \text{ by (406)}$$

$$= \frac{p_0 v_0 E}{Jv\left(\frac{dH}{dv}\right)_t}. \tag{407}$$

If H denote the quantity of heat evolved by a portion of gas while being compressed from volume V to volume V' at temperature t,

$$H = \int_{V'}^{V}\left(\frac{dH}{dv}\right)_t dv$$

$$= \int_{V'}^{V} \frac{p_0 v_0 E}{J\mu v}\, dv, \text{ by (407)}$$

$$= \frac{p_0 v_0 E}{J\mu}\int_{V'}^{V}\frac{dv}{v}$$

$$\left.\begin{aligned} &= \frac{p_0 v_0 E}{J\mu}\log\frac{V}{V'} \\ &= \frac{Epv}{J\mu\left[1 + Et\right]}\log\frac{V}{V'} \end{aligned}\right\} \tag{408}$$

Let W denote the work performed during this compression. Then

$$W = \int_{V'}^{V} p_t\, dv$$

$$= \int_{V'}^{V}\left[\frac{p_0 v_0 (1 + Et)}{v}\right]_t dv, \text{ by (405)}$$

$$= p_0 v_0 (1 + Et)\int_{V'}^{V}\frac{dv}{v}$$

$$\left.\begin{aligned} &= p_0 v_0 (1 + Et) \log \frac{V}{V'} \\ &= pv \log \frac{V}{V'}. \end{aligned}\right\} \tag{409}$$

If we assume with Mayer, as Thomson and Joule have proved experimentally that we may do, that the work of compression in this case is the dynamical equivalent of the heat emitted by the gas during compression while kept at constant temperature, we have

$$W = JH; \tag{410}$$

$$\therefore \quad pv \log \frac{V}{V'} = J \frac{Epv}{J\mu[1 + Et]} \log \frac{V}{V'}; \tag{411}$$

$$\left.\begin{aligned} \therefore \quad \mu &= \frac{E}{1 + Et} \\ &= \frac{1}{\frac{1}{E} + t}. \end{aligned}\right\} \tag{412}$$

Hence, if we define absolute temperature as the reciprocal of Carnot's function, we have

$$\begin{aligned} \frac{1}{E} + t &= \frac{1}{\mu} \\ &= \text{absolute temperature} \\ &= \tau. \end{aligned} \tag{413}$$

Conversely, if we define absolute temperature as

$$\tau = \frac{1}{E} + t,$$

we have

$$\mu = \frac{1}{\tau},$$

or

$$\tau = \frac{1}{\mu}. \tag{414}$$

That is, absolute temperature is the reciprocal of Carnot's function.

Let λ denote the quantity of heat which will convert σ units of volume of water into 1 unit volume of steam of the same temperature.

Then if dH units of heat be added to a body consisting of water and steam whose whole mass is one pound, and whose temperature is t,

$\frac{dH}{\lambda}$ units of volume of steam are formed by the evaporation of $\sigma \cdot \frac{dH}{\lambda}$ units of volume of water.

Hence the increase of volume of the body will be

$$dv = \frac{dH}{\lambda} - \sigma \cdot \frac{dH}{\lambda}$$

$$= (1 - \sigma) \frac{dH}{\lambda};$$

$$\therefore \quad \left(\frac{dH}{dv}\right)_t = \frac{\lambda}{1 - \sigma}.$$

But

$$M = \left(\frac{dH}{dv}\right)_t;$$

$$\therefore \quad M = \frac{\lambda}{1 - \sigma}. \tag{415}$$

Hence from (345),

$$\mu = \frac{1}{JM} \left(\frac{dp}{dt}\right)_v$$

$$= \frac{1 - \sigma}{J\lambda} \left(\frac{dp}{dt}\right)_v. \tag{416}$$

Let the working body consist of x units of mass of a higher form, and $1 - x$ units of a lower form, at temperature t and volume v.

Putting V_1 and V_2 for the volumes of unit mass of the substance in the higher and lower forms, we have

$$v = V_1 x + V_2(1 - x). \tag{417}$$

Put λ for the latent heat of unit mass of the higher form, that is, the quantity of heat which will convert a unit mass of the lower form into the higher form without changing its temperature.

Hence if the addition of δH units of heat to the body, kept at temperature t, convert δx units of mass from the lower to the higher form, we shall have

$$\delta H = \lambda \delta x;$$

$$\therefore \quad \left(\frac{dH}{dx}\right)_t = \lambda.$$

But from (417),

$$\left(\frac{dv}{dx}\right)_t = V_1 - V_2;$$

$$\therefore \quad M = \left(\frac{dH}{dv}\right)_t$$

$$= \left(\frac{dH}{dx}\right)_t \div \left(\frac{dv}{dx}\right)_t$$

$$= \frac{\lambda}{V_1 - V_2}. \tag{418}$$

Hence from (345) and (418),

$$\mu = \frac{1}{JM}\left(\frac{dp}{dt}\right)_v$$

$$= \frac{V_1 - V_2}{J\lambda}\left(\frac{dp}{dt}\right)_v. \tag{419}$$

Now if σ denote the ratio of the density of the higher form to that of the lower,

$$\rho_1 = \sigma \rho_2.$$

But
$$V_1\rho_1 = 1 = V_2\rho_2 = \frac{V_2\rho_1}{\sigma}.$$

Hence (419) becomes

$$\mu = \frac{V_1\rho_1 - V_2\rho_1}{J\lambda\rho_1}\left(\frac{dp}{dt}\right)_v$$
$$= \frac{1-\sigma}{J\lambda\rho_1}\left(\frac{dp}{dt}\right)_v. \tag{420}$$

With the same substitutions (418) becomes

$$M = \frac{\lambda\rho_1}{1-\sigma}, \tag{421}$$

which is the same as (126) which we promised to prove.

These results might have been deduced from those immediately preceding by putting $\lambda\rho_1$ for λ, because the latent heat of unit mass multiplied by the density of the higher form will give the latent heat of unit volume of the higher form.

If we put H and H' for the quantities of heat taken in and given out by a reversible heat engine, working through a Carnot's cycle, at the temperature τ and τ', and if we define absolute temperature as Thomson does, we have

$$\frac{H}{\tau} = \frac{H'}{\tau'} = \frac{H-H'}{\tau-\tau'}; \tag{422}$$

$$\therefore \quad W = \text{work of cycle}$$
$$= J(H-H')$$
$$= JH\frac{\tau-\tau'}{\tau}. \tag{423}$$

That is, the fraction $\frac{\tau-\tau'}{\tau}$ of the heat taken in at the source is convertible into work by a reversible engine.

Of course any actual heat engine will convert a smaller fraction than this into work.

From (385), (384),

$$\left.\begin{aligned}\left(\frac{dt}{dv}\right)_\phi &= -\frac{M}{N}\\ &= -\frac{K-N}{N}\left(\frac{dt}{dv}\right)_p\\ &= -\frac{K-N}{N}\frac{p}{p_0v_0E}\\ &= -\frac{K-N}{N}\frac{1+Et}{Ev_0}\end{aligned}\right\}\text{ from (405)}$$

$$\therefore\quad \frac{1}{\frac{1}{E}+t}\cdot\left(\frac{dt}{dv}\right)_\phi = -\left(\frac{K}{N}-1\right)\frac{1}{v}. \qquad (424)$$

Integrating between limits, supposing $\frac{K}{N}$ to be constant, we have

$$\left.\begin{aligned}\log\frac{\frac{1}{E}+t}{\frac{1}{E}+t'} &= \left(\frac{K}{N}-1\right)\log\frac{v'}{v};\\ \therefore\quad \frac{\frac{1}{E}+t}{\frac{1}{E}+t'} &= \left(\frac{v'}{v}\right)^{\frac{K}{N}-1}.\\ &= \left(\frac{v'}{v}\right)^{\cdot 41},\\ \text{or}\qquad \frac{273+t}{273+t'} &= \left(\frac{v'}{v}\right)^{\cdot 41}.\end{aligned}\right\} \qquad (425)$$

Now:
$$\left.\begin{aligned}\frac{p'v'}{pv} &= \frac{p_0v_0(1+Et')}{p_0v_0(1+Et)}\\ &= \frac{1+Et'}{1+Et} = \frac{\frac{1}{E}+t'}{\frac{1}{E}+t};\\ \therefore\quad \frac{v'}{v} &= \frac{p}{p'}\cdot\frac{\frac{1}{E}+t'}{\frac{1}{E}+t}.\end{aligned}\right\}\qquad(426)$$

Hence from this and (425) we get

$$\frac{pv}{p'v'} = \left(\frac{v'}{v}\right)^{\frac{K}{N}-1};$$

$$\therefore\quad \frac{p}{p'} = \left(\frac{v'}{v}\right)^{\frac{K}{N}} = \left(\frac{v'}{v}\right)^{1\cdot41};\qquad(427)$$

and
$$\frac{\frac{1}{E}+t}{\frac{1}{E}+t'} = \left[\frac{p}{p'}\cdot\frac{\frac{1}{E}+t'}{\frac{1}{E}+t}\right]^{\frac{K}{N}-1};$$

$$\left.\begin{aligned}\therefore\quad \left(\frac{\frac{1}{E}+t}{\frac{1}{E}+t'}\right)^{\frac{K}{N}} &= \left(\frac{p}{p'}\right)^{\frac{K}{N}-1},\\ \text{or}\quad \left(\frac{273+t}{273+t'}\right)^{1\cdot41} &= \left(\frac{p}{p'}\right)^{\cdot41}.\end{aligned}\right\}\qquad(428)$$

These last two results may be got independently from (389) and (387), in the same way as (425) was got from (385). (425), (427) and (428) are true for gases only.

CHAPTER XVI.

REVERSIBILITY AND IRREVERSIBILITY.

ANY transformation which a body can experience is either reversible or irreversible.

We have already, in Thomson's words (ch. III.), given a definition of reversibility. But, as it was given with respect to a whole cycle, it may be as well to remould it so as to adapt it to any transformation.

DEFINITION.—*If a body experience a transformation or series of transformations of such a nature that the whole process can be performed in exactly the reverse order; and if, at each point of the reverse operation, the physical and mechanical agencies are all of the same magnitude as at the same point of the direct operation, but reversed in direction, the transformation is said to be reversible.*

It is worthy of remark that the *possibility* of the reversal of the transformation depends on *two sets of conditions:* namely, (1) the nature of the transformations the body experiences; and (2) the external conditions under which the transformations take place.

It may therefore happen that a transformation which is irreversible with the given external conditions might be reversible, if for the given external conditions we could substitute other external conditions which would be equivalent to the given external conditions during the direct transformation, but not so while the reverse transformation is taking place.

That is to say, a body may experience a transformation which is not *absolutely* irreversible but only *relatively* so, owing to the nature of the existing external conditions.

For example, a heat engine in working through a cycle of changes always loses more or less heat by conduction and radiation, which, with existing external circumstances, would not be restored to it if we attempted to reverse the cycle of changes. Yet the cycle of changes might be such that we could reverse it if we were to substitute for the existing external conditions others equivalent to them while the engine is working directly, but which, when the engine is worked backwards, would, at each point of the process, give heat to or take heat from the working body at exactly the same rate as at the same point of the direct cycle heat was taken from or given to the working body.

This reasoning is not invalidated by the fact that such substituted external conditions may *not be actually realizable*, any more than the reasoning on Carnot's cycle is invalidated by the fact that the conditions necessary for its production are not exactly realizable. All that is necessary is that such external conditions should be *conceivable* and capable of being approximated to.

A transformation, which under existing external conditions is irreversible, but which may be made reversible by the substitution of other external conditions, may be said to be *conditionally irreversible.*

Again, a body may undergo a process of transformation which could not be made reversible by the substitution of any conceivable external conditions for the existing ones. Such a transformation may be said to be *intrinsically irreversible.*

We have an example of such a transformation in that experienced by the air in rushing from one vessel into

another exhausted vessel in Joule's experiment. Of course the air could be restored to its original condition, but not by a process the reverse of the direct transformation.

The transformation experienced by the air rushing through the porous plug in the Joule-Thomson experiments is another example of an intrinsically irreversible process of transformation.

In Chapter III. five conditions were mentioned as essential to the reversibility of a cycle of operations.*

A cycle in which the fifth condition only is violated is conditionally irreversible.*

A cycle which violates one or more of the first four conditions is intrinsically irreversible.*

In Chapter VI. we have shown that in any cycle satisfying the first four of the conditions mentioned in Chapter III.,

$$\left.\begin{aligned} &\Sigma\left(He^{-\int\mu dt}\right) = 0, \\ \text{or}\quad &\int e^{-\int\mu dt}\, dH = 0; \\ \text{or in the absolute scale,}\quad & \\ &\Sigma\left(\frac{H}{t}\right) = 0, \\ \text{or}\quad &\int \frac{dH}{t} = 0; \end{aligned}\right\} \qquad (429)$$

where the summation or integration is to be carried round the whole cycle.

Hence these equations are true for *all cycles except intrinsically irreversible ones.*

No diagram can be drawn to represent an intrinsically irreversible process of transformation.

* These statements are true of transformations whether cyclical or not.

But a diagram might be drawn for each elementary portion of the body; and the above formulæ will be true for each element, provided the heat generated in it by friction, external and internal, be included in the integral.

If the average of all these diagrams could be drawn, it might be looked upon as the diagram for the whole body; and the foregoing equations would, under the same supposition as to the heat generated by friction, still be true.

There might be a difficulty with regard to the meaning of t at a point in the course of such a transformation, but it could be found from the known volume and intrinsic energy of the body at that point. The intrinsic energy could be determined thus:—

$$E = E_1 + J(Q) - (W), \tag{430}$$

where E_1 = intrinsic energy at beginning of the transformation;

(Q) = the heat received by the body from without from the beginning to the point;

and (W) = the external work done by the body from the beginning of the transformation to the point arrived at.

If an isomeg and an isenerg be drawn corresponding to the known volume v, and energy E, the point where these intersect will be upon a certain isotherm corresponding to the temperature t.

So far as the integration is concerned, however, there is no need for this, as the value of

$$\int e^{-\int \mu dt} dH,$$

or

$$\int \frac{dH}{t},$$

is the same for all transformations represented by thermo-

grams having the same extremities, so that any one of these thermograms might be substituted for any other, so far as this integration is concerned.

The simplest substitution to make would be to put for the average thermogram a thermogram formed by an isothermal through one extremity and an isentrope through the other.

It is therefore evident that if the heat generated by friction be omitted, the value of the integral will be diminished.

Hence for an intrinsically irreversible cycle,

$$\left.\begin{aligned} &\int e^{-\int \mu dt}\, dH < 0, \\ \text{or} \quad &\int \frac{dH}{t} \qquad < 0, \end{aligned}\right\} \tag{431}$$

if only the heat crossing the surface of the enclosing vessel is taken account of.

It will also be evident that, for a conditionally irreversible cycle,

$$\int \frac{dH}{t} < 0, \tag{432}$$

if t, instead of denoting the temperature of the working body at which it receives the heat dH, denote the temperature of the body from which the working body receives this heat, for, since the former temperature is less than the latter, $\frac{dH}{t}$ will be diminished.

Also, if dH be negative, *i.e.* if the working body be giving out heat to an external body, the temperature of the working body will be greater than that of the external body. Hence the value of $\frac{dH}{t}$ will be *algebraically* diminished by

putting the temperature of the outside body instead of that of the working body.

Hence such changes will diminish the value of the integral;

$$\therefore \int \frac{dH}{t} < 0.$$

Shortly then:—Every transformation is either *reversible*, *conditionally irreversible*, or *intrinsically irreversible*.

If t denote the temperature of the *working body*,

$$\left.\begin{aligned} &\Sigma\left(\frac{H}{t}\right) = 0, \\ \text{or} \quad &\int \frac{dH}{t} = 0, \end{aligned}\right\} \tag{433}$$

for *every reversible cycle* of transformations, and also for *every conditionally irreversible cycle*.

For an intrinsically irreversible cycle, if t denote the temperature of an element dm of the working substance, and dH the heat it receives *from without*—

$$\left.\begin{aligned} &\text{then for each element,} \\ &\int \frac{dH}{t} < 0; \\ &\text{and for the whole body,} \\ &\int dm \int \frac{dH}{t} < 0. \end{aligned}\right\} \tag{434}$$

But if dH include both heat received by dm from without, and also heat produced by fluid friction within it—

$$\left.\begin{aligned} &\text{then for the element,} \\ &\int \frac{dH}{t} = 0; \\ &\text{and for the whole body,} \\ &\int dm \int \frac{dH}{t} = 0. \end{aligned}\right\} \tag{435}$$

CHAPTER XVII.

THERMODYNAMIC MOTIVITY AND DISSIPATION.

If the lowest available temperature be denoted by t_0, then the greatest possible quantity of work which can be got from a quantity of heat dH obtained from a body of temperature t is

$$JdH\left\{1 - e^{-\int_{t_0}^{t}\mu dt}\right\} \text{ for any scale,}$$

or

$$JdH\left(1 - \frac{t_0}{t}\right) \text{ for the absolute scale.}$$

This availability for doing work possessed by the quantity of heat dH, in virtue of its being in a body of temperature t, has been called by Sir William Thomson its *Motivity*.

It is evident, therefore, that when a quantity of heat dH leaves a body of temperature t_1, and enters another of lower temperature t_2, its motivity diminishes from

$$JdH\left\{1 - e^{+\int_{t_1}^{t_0}\mu dt}\right\}, \text{ or } JdH\left(1 - \frac{t_0}{t_1}\right),$$

to

$$JdH\left\{1 - e^{+\int_{t_2}^{t_0}\mu dt}\right\}, \text{ or } JdH\left(1 - \frac{t_0}{t_2}\right).$$

Hence its loss of motivity is

$$JdH\left\{e^{\int_{t_2}^{t_0}\mu dt} - e^{\int_{t_1}^{t_0}\mu dt}\right\},$$

or

$$Jt_0dH\left(\frac{1}{t_2} - \frac{1}{t_1}\right).$$

Again, if dH denote the heat given to an engine by external matter whose temperature is t, then in a cycle of the engine the external matter from which it receives its heat will have lost motivity of amount,

$$J\int\left\{1-e^{-\int_{t_0}^{t}\mu dt}\right\}dH,$$

or

$$J\int\left(1-\frac{t_0}{t}\right)dH,$$

where the integration extends over the cycle.

But if the engine were reversible, the work done during the cycle would be

$$J\int dH.$$

Hence the needless loss of motivity will be

$$J\int\left\{1-e^{-\int_{t_0}^{t}\mu dt}\right\}dH-J\int dH=-J\int e^{-\int_{t_0}^{t}\mu dt}\,dH,$$

or

$$J\int\left(1-\frac{t_0}{t}\right)dH-J\int dH=-Jt_0\int\frac{dH}{t}.$$

This, then, is Thomson's expression for the needless loss of motivity of the system which communicates heat to and takes heat from the engine in one cycle of the engine. Needless loss of motivity is called by Thomson *dissipated energy*.

It ought to be carefully remembered that, in these integrals, *t is not the temperature of the working body, but of the external matter which communicates dH to the working body.*

Hence, since at the end of Chapter XVI. it has been shown that $\int\frac{dH}{t}<0$ for irreversible cycles, there will be real dissipation of energy for such a cycle.

But for a reversible cycle $\int\frac{dH}{t}=0$.

Hence for such a cycle there is no dissipation of energy.

The following interesting problems on motivity are due to Thomson and Tait:—

(1). Find the motivity of a uniform mass m at uniform temperature t, the lowest available temperature being t_0.

Let c denote the specific heat of the substance. Then the motivity is evidently

$$\begin{aligned}\text{Motivity} = mL_{\delta t=0}\Big\{ & c_t\delta t\left(1-\frac{t_0}{t}\right)+c_{t+\delta t}\delta t\left(1-\frac{t_0}{t+\delta t}\right)\\ & + c_{t+2\delta t}\delta t\left(1-\frac{t_0}{t+2\delta t}\right)+\ldots\\ & + c_{t+n\delta t}\delta t\left(1-\frac{t_0}{t+n\delta t}\right)\Big\}\\ & = m\int_{t_0}^{t}\left[1-\frac{t_0}{t}\right]cdt, \qquad (436)\end{aligned}$$

where $$t + n\delta t = t_0.$$

If c is independent of the temperature, this becomes

$$\text{Motivity} = mc\left\{(t-t_0) - t_0\log\frac{t}{t_0}\right\}.$$

Cor.—The loss of motivity of m, if reduced from temperature t to temperature T, is

$$\begin{aligned}(M)_t - (M)_T &= m\left\{\int_{t_0}^{t}\left(1-\frac{t_0}{t}\right)cdt - \int_{t_0}^{T}\left(1-\frac{t_0}{t}\right)cdt\right\}\\ &= m\int_{T}\left(1-\frac{t_0}{t}\right)cdt. \qquad (437)\end{aligned}$$

(2). "Find the mechanical energy or work derivable from a body, given with its different parts at different temperatures, by the equalization of the temperature throughout to one common temperature, T, by means of perfect thermodynamic engines."

The elementary portion of work done by a perfect heat engine working between the temperatures t and T, on receiving the quantity of heat $-cdmdt$ from dm at temperature t, is

$$-Jcdmdt\left(1-\frac{T}{t}\right).$$

Hence the total work in reducing the temperature of dm from t to T is

$$Jdm\int_T^t\left(1-\frac{T}{t}\right)cdt.$$

Therefore the total work done in reducing the temperature of all the parts of the body to temperature T is

$$W=J\int dm\int_T^t\left(1-\frac{T}{t}\right)cdt. \qquad (438)$$

If T be the temperature of an external body so great that its temperature is practically unaffected by the heat it receives from the body in question, the above may be called the external thermodynamic motivity of the body, provided T be the lowest available temperature.

If, however, the body be enclosed in a non-conducting envelope, the equivalent of this will be to suppose that T, the temperature of the external body, is such that on the whole the external body receives no heat from the body in question; that is, we suppose the external body to act as a source to the thermodynamic engines to which some parts of the given body act as refrigerators, while at the same time it acts as a refrigerator to the thermodynamic engines to which the remaining portions of the given body act as sources, and its temperature T is to be such that the heat it gives up to the former set of engines is exactly equal to that which it receives from the latter set.

If the external body acts as a source which gives to the engine a quantity such that the refrigerator dm receives $cdmdt$,

causing its temperature to rise by dt, the quantity of heat parted with by the source will be

$$cdmdt \cdot \frac{T}{t}.$$

Again, if the external body act as a refrigerator to a heat engine receiving the quantity of heat $-cdmdt$, from the mass dm, causing its temperature to fall $+dt$, the quantity of heat received by the external body on this account will be

$$-cdmdt\frac{T}{t}.$$

Hence the total heat received by the external body will be

$$-\int dm \int_t^T \frac{T}{t} cdt,$$

or

$$\int dm \int_T^t \frac{T}{t} cdt.$$

But this by hypothesis is to be zero.

Hence

$$\left.\begin{aligned} &\int dm \int_T^t \frac{T}{t} cdt = 0, \\ \text{or} \quad &\int dm \int_T^t \frac{cdt}{t} = 0. \end{aligned}\right\} \qquad (439)$$

Hence the quantity of work obtainable in these circumstances will be

$$\begin{aligned} W &= J\int dm \int_T^t \left(1 - \frac{T}{t}\right) cdt \\ &= J\int dm \int_T^t cdt - JT\int dm \int_T^t \frac{cdt}{t} \\ &= J\int dm \int_T^t cdt. \end{aligned} \qquad (440)$$

This is called the *internal thermodynamic motivity* of the body.

Cor. 1.—If c be independent of t, these results become

$$\left.\begin{aligned} &\int cdm \log \frac{t}{T} = 0, \\ \text{or} \qquad &T = e^{\frac{\int cdm \log t}{\int cdm}}, \end{aligned}\right\} \tag{441}$$

and
$$W = J \int cdm\,(t - T). \tag{442}$$

Cor. 2.—If the body be also homogeneous, these results become

$$T = e^{\frac{\int dm \log t}{m}}, \tag{443}$$

and
$$W = Jc\,\{\int tdm - m\,.\,T\}. \tag{444}$$

Cor. 3.—If the body consists of several parts m_1, m_2, &c., respectively of uniform temperatures t_1, t_2, &c., and specific heats c_1, c_2, &c., and if c_1, c_2, &c., do not depend on temperature, the results will become

$$\begin{aligned} T &= e^{\frac{m_1c_1 \log t_1 + m_2c_2 \log t_2 + \&c.}{m_1c_1 + m_2c_2 + \&c.}} \\ &= e^{\frac{m_1c_1 \log t_1}{\Sigma(mc)}}\,.\,e^{\frac{m_2c_2 \log t_1}{\Sigma(mc)}}\,.\,.\,.\,.\,. \\ &= e^{\log\left(t_1^{\frac{m_1c_1}{\Sigma(mc)}}\right)}\,.\,e^{\log\left(t_2^{\frac{m_2c_2}{\Sigma(mc)}}\right)}\,.\,.\,.\,.\,. \\ &= t_1^{\frac{m_1c_1}{\Sigma(mc)}}\,.\,t_2^{\frac{m_2c_2}{\Sigma(mc)}}\,.\,.\,.\,.\,. \\ &= \left\{t_1^{m_1c_1}\,.\,t_2^{m_2c_2}\,.\,.\,.\,.\,.\right\}^{\frac{1}{\Sigma(mc)}}, \end{aligned} \tag{445}$$

and $$W = J\{c_1m_1(t_1 - T) + c_2m_2(t_2 - T) + \&c.\}$$
$$= J\{[c_1m_1t_1 + c_2m_2t_2 + \&c.] - T[c_1m_1 + c_2m_2 + \&c.]\}$$
$$= J\{\Sigma(cmt) - T\Sigma(cm)\}. \qquad (446)$$

If the masses are n in number, and the same in every respect except temperature, these reduce to

$$T = \sqrt[n]{t_1 . t_2 . t_3 . . . . t_n}, \qquad (447)$$

and $$W = Jcm\{(t_1 + t_2 + . . . + t_n) - n\sqrt[n]{t_1 . t_2 . t_3 . . . t_n}\}$$
$$= Jcmn\left\{\frac{t_1 + t_2 + . . . + t_n}{n} - \sqrt{t_1 . t_2 . t_3 . . . t_n}\right\}$$
$$= Jcmn\{T' - T\}. \qquad (448)$$

Hence the motivity $\propto T' - T$, where T' is the arithmetic mean of $t_1, t_2, . . . , t_n$, and T their geometric mean.

(3). "The motivity of a system is equal to the sum of the motivities of its parts, together with their mutual motivity, when their individual motivities have been exhausted."

Let the component bodies of the system be m_1, m_2, &c., and let T_1, T_2, &c., be their temperatures when their individual motivities have been exhausted, and let t_0 be the temperature of the system when all its motivity has been exhausted. Then

$$\text{Motivity of system} = \int dm_1 \int_{t_0}^{t_1}\left(1 - \frac{t_0}{t_1}\right)c_1dt_1$$
$$+ \int dm_2 \int_{t_0}^{t_2}\left(1 - \frac{t_0}{t_2}\right)c_2dt_2 + \&c.$$
$$= \Sigma\left\{\int dm \int_{t_0}^{t}\left(1 - \frac{t_0}{t}\right)cdt\right\}$$
$$= \Sigma\left\{\int dm \int_{T}^{t}\left(1 - \frac{t_0}{t}\right)cdt\right.$$
$$\left. + \int dm \int_{t_0}^{T}\left(1 - \frac{t_0}{t}\right)cdt\right\}$$

$$\text{Motivity of system} = \Sigma \left\{ \int dm \int_T^t cdt + \int dm \int_{t_0}^T \left(1 - \frac{t_0}{t}\right) cdt \right\}$$

$$= \Sigma \int dm \int_T^t cdt + \Sigma \int dm \int_{t_0}^T \left(1 - \frac{t_0}{t}\right) cdt$$

= Sum of individual motivities of parts

+ Mutual motivity of parts after their individual motivities have been exhausted. (449)

Since all other forms of energy naturally tend to degenerate into heat, and since bodies of different temperatures and unequally heated parts of the same body tend by means of radiation and conduction to attain the same temperature, it is evident that the motivity of the universe tends to zero.

This is the grand principle of the Dissipation of Energy of the Universe first stated by Thomson.

Clausius not long afterwards stated the principle in a somewhat modified form, namely:—

The entropy of the universe tends towards a maximum.

The same reasoning will prove this. For when another form of energy changes into heat in some body or system, the entropy of the body or system is thereby increased; and when a quantity of heat dH leaves a particle whose temperature is t_1, and passes undiminished into another whose temperature is t_2, there is an increase of entropy of value,

$$\frac{dH}{t_2} - \frac{dH}{t_1}.$$

So that there is a continual increase of entropy going on which will only cease when all the energy of the universe has attained the form of uniform temperature heat.

CHAPTER XVIII.

ON THE ENTROPY, ETC., OF A BODY OR SYSTEM OF BODIES WHOSE TEMPERATURE AND PRESSURE ARE NOT THE SAME AT ALL PARTS OF THE BODY OR SYSTEM.

WHEN the temperature and pressure are the same at all points of a body or system, the entropy of the body or system may be defined, in the words of Clerk Maxwell, as "*a property of a body, expressed as a measurable quantity, such that when there is no communication of heat this quantity remains constant.*"

In the case where the temperature and pressure are not the same at all points of the body or system, writers on this subject all, as far as I know, define *the entropy of the body or system* as *the sum of the entropies of its parts*, which seems to me as unwarrantable as to define *the temperature of a body or system* as *the sum of the temperatures of its parts.*

In order to effect the calculation of the entropy of a body or system in this way of dealing with the property, it is necessary to speak of *entropy per unit mass*, which again seems to me as unwarrantable as to speak of *temperature per unit mass.*

Taking this view of the subject, Clerk Maxwell defines

the entropy of the system of bodies m_1, m_2, &c., whose entropies per unit mass are ϕ_1, ϕ_2, &c., as

$$= m_1\phi_1 + m_2\phi_2 + \&c. = \Sigma(m\phi) = \Phi. \qquad (450)$$

He then proceeds to show that if a quantity of heat H pass from m_1 to m_2, the entropy of the system increases by the quantity

$$H\left(\frac{1}{\tau_2} - \frac{1}{\tau_1}\right).$$

That is to say, *the entropy of a system can increase without any heat passing into or out of the system.*

This appears to me to be *quite foreign to the primary notion of entropy* given in the definition at the beginning of this Chapter.

I cannot help thinking this definition ought to apply to *any* body or system, and that the entropy of such a system as we are at present dealing with ought to be calculated or expressed by a formula which will satisfy this definition. So that if H units of heat pass from m_1 to m_2, there should be no change in the entropy of the system, although the entropy of m_1 decreases by $\frac{JH}{m_1\tau_2}$, while that of m_2 increases by $\frac{JH}{m_2\tau_2}$.

A formula which satisfies this condition is

$$\phi = \frac{\tau_1 m_1\phi_1 + \tau_2 m_2\phi_2 + \&c.}{\tau_1 m_1 + \tau_2 m_2 + \&c.}. \qquad (451)$$

For if m_1 lose H units of heat, the quantity lost by each unit of mass will be $\frac{H}{m_1}$, and the loss of entropy will be $\frac{JH}{m_1\tau_1}$. Similarly, the gain of entropy of m_2, on receiving these H units from m_1 will be $\frac{JH}{m_2\tau_2}$. Hence the entropies of m_1 and

m_2 will now be $\phi_1 - \dfrac{JH}{m_1\tau_1}$ and $\phi_2 + \dfrac{JH}{m_2\tau_2}$,

and the entropy of the system will become

$$\frac{\tau_1 m_1\left[\phi_1 - \dfrac{JH}{m_1\tau_1}\right] + \tau_2 m_2\left[\phi_2 + \dfrac{JH}{\tau_2 m_2}\right] + \tau_3 m_3\phi_3 + \&c.}{\tau_1 m_1 + \tau_2 m_2 + \tau_3 m_3 + \&c.}$$

or $$\frac{(\tau_1 m_1\phi_1 - JH) + (\tau_2 m_2\phi_2 + JH) + \tau_3 m_3\phi_3 + \&c.}{\tau_1 m_1 + \tau_2 m_2 + \tau_3 m_3 + \&c.}$$

or $$\frac{\tau_1 m_1\phi_1 + \tau_2 m_2\phi_2 + \tau_3 m_3\phi_3 + \&c.}{\tau_1 m_1 + \tau_2 m_2 + \tau_3 m_3 + \&c.}$$

which is the same as it was before the transference took place.

This mode of treatment has the further most important advantage, that it renders Thomson's or Clausius' extension of the Second Law true for any body or system which passes through *any series of changes, whether reversible or not*, and returns to its initial state, provided we define the *temperature of the system* by the following equation:—

$$\tau = \frac{m_1\tau_1 + m_2\tau_2 + \&c.}{m_1 + m_2 + \&c.} \tag{452}$$

Hence $m_1\tau_1 + m_2\tau_2 + \&c. = (m_1 + m_2 + \&c.)\,\tau$;

$\therefore$ (451) becomes

$$\phi = \frac{\tau_1 m_1\phi_1 + \tau_2 m_2\phi_2 + \&c.}{(m_1 + m_2 + \&c.)\,\tau} \tag{453}$$

Suppose $H = H_1 + H_2 + \&c.$ units of heat are added to the system, m_1, m_2, &c., receiving respectively H_1, H_2, &c. units, and that the entropy of the system becomes ϕ', while its temperature τ remains unchanged.

Then
$$\phi' = \frac{\tau_1 m_1 \phi_1' + \tau_2 m_2 \phi_2' + \&c.}{(m_1 + m_2 + \&c.)\,\tau}$$
$$= \frac{\tau_1 m_1\left(\phi_1 + \frac{JH_1}{m_1\tau_1}\right) + \tau_2 m_2\left(\phi_2 + \frac{JH_2}{m_2\tau_2}\right) + \&c.}{(m_1 + m_2 + \&c.)\,\tau}$$
$$= \frac{(\tau_1 m_1 \phi_1 + \tau_2 m_2 \phi_2 + \&c.) + J(H_1 + H_2 + \&c.)}{(m_1 + m_2 + \&c.)\,\tau}$$
$$= \frac{(\tau_1 m_1 \phi_1 + \tau_2 m_2 \phi_2 + \&c.) + JH}{(m_1 + m_2 + \&c.)\,\tau}$$
$$= \phi + \frac{JH}{(m_1 + m_2 + \&c.)\,\tau}.$$

Hence the increase of entropy caused by the addition of H units of heat to the system is

$$\phi' - \phi = \frac{JH}{m\tau}, \tag{454}$$

where m denotes the mass of the system, *i.e.*

$$m = m_1 + m_2 + \&c.$$

Let now $H, H', H'', H''', \ldots\ldots, H^{(n-1)}$ units of heat be added in succession to the system, causing it to pass from entropy ϕ to ϕ', ϕ' to ϕ'', ϕ'' to ϕ''', $\ldots\ldots$, $\phi^{(n-1)}$ to ϕ^{n}, at temperatures $\tau, \tau', \tau'', \tau''', \ldots\ldots$, the changes from τ to τ', τ' to τ'', τ'' to τ''', $\ldots\ldots$, $\tau^{(n-1)}$ to τ^{n} taking place while the entropy remains at the constant values $\phi', \phi'', \phi''', \ldots\ldots, \phi^{(n)}$. Then the total change of entropy will be

$$\phi^{(n)} - \phi = (\phi' - \phi) + (\phi'' - \phi') + (\phi''' - \phi'') + \ldots + (\phi^{(n)} - \phi^{(n-1)})$$
$$= \frac{JH}{m\tau} + \frac{JH'}{m\tau'} + \frac{JH''}{m\tau''} + \ldots + \frac{JH^{(n-1)}}{m\tau^{(n-1)}}. \tag{455}$$

Now if the system has returned to its initial state,

$$\phi^{(n)} = \phi\,;$$

$$\therefore \quad \frac{JH}{m\tau} + \frac{JH'}{m\tau'} + \frac{JH''}{m\tau''} + \ldots + \frac{JH^{(n-1)}}{m\tau^{(n-1)}} = 0\,;$$

$$\therefore \quad \frac{H}{\tau} + \frac{H'}{\tau'} + \frac{H''}{\tau''} + \ldots + \frac{H^{(n-1}}{\tau^{(n-1)}} = 0\,; \qquad (456)$$

which is Thomson's or Clausius' Extension of the Second Law.

With regard to v and E, the average volume and energy per unit mass of the system, I think there can be no doubt as to the proper way of expressing them being

$$v = \frac{m_1 v_1 + m_2 v_2 + \&c.}{m_1 + m_2 + \&c.} \qquad (457)$$

$$= \frac{m_1 v_1 + m_2 v_2 + \&c.}{m}$$

and

$$E = \frac{m_1 E_1 + m_2 E_2 + \&c.}{m_1 + m_2 + \&c.}$$

$$= \frac{m_1 E_1 + m_2 E_2 + \&c.}{m}. \qquad (458)$$

But with regard to the average pressure of the system, there might be different opinions as to the mode of expressing it.

I think that it ought to be expressed thus:—

$$\left.\begin{aligned} p &= \left[\frac{m_1 p_1 \delta v_1 + m_2 p_2 \delta v_2 + \&c.}{m_1 \delta v_1 + m_2 \delta v_2 + \&c.}\right]_{\tau_1,\, \tau_2,\, \&c.} \\ &= \left[\frac{m_1 p_1 \delta v_1 + m_2 p_2 \delta v_2 + \&c.}{m \delta v}\right]_{\tau_1,\, \tau_2,\, \&c.} \end{aligned}\right\} \qquad (459)$$

My reason for thinking so is the following:—

The equation $\qquad \tau\delta\phi = \delta E + p\delta v,$

which is a fundamental equation for a body or system in

which the pressure and temperature are the same throughout the body or system, ought I think to be true for the system we are dealing with.

Hence
$$p = \frac{\tau\delta\phi - \delta E}{\delta v}. \tag{460}$$

If now we suppose the changes in the system to take place without altering τ_1, τ_2, &c., the temperatures of its parts, we shall have from (453)

$$\tau\delta\phi = \frac{\tau_1 m_1 \delta\phi_1 + \tau_2 m_2 \delta\phi_2 + \&c.}{m}; \tag{461}$$

and from (458)

$$\delta E = \frac{m_1 \delta E_1 + m_2 \delta E_2 + \&c.}{m}; \tag{462}$$

and therefore (460) becomes

$$p = \frac{m_1[\tau_1 \delta\phi_1 - \delta E_1]_{\tau_1} + m_2[\tau_2 \delta\phi_2 - \delta E_2]_{\tau_2} + \&c.}{m\delta v}$$

$$= \frac{m_1(p_1 \delta v_1)_{\tau_1} + m_2(p_2 \delta v_2)_{\tau_2} + \&c.}{m\delta v}$$

$$= \left[\frac{m_1 p_1 \delta v_1 + m_2 p_2 \delta v_2 + \&c.}{m\delta v}\right]_{\tau_1,\, \tau_2,\, \&c.} \tag{463}$$

the suffixes τ_1, τ_2, &c., denoting that the changes of volume δv_1, δv_2, &c., are to be isothermal.

Now as the changes of volume δv_1, δv_2, &c., are quite *arbitrary*, except that they are to take place *isothermally*, we may assume the following condition :—

$$\left.\begin{aligned} &\frac{\delta v_1}{v_1} = \frac{\delta v_2}{v_2} = \ldots\ldots = \frac{\delta v}{v}; \\ \text{and} \quad &\therefore \quad \delta v_1 = \frac{v_1}{v}\delta v, \quad \delta v_2 = \frac{v_2}{v}\delta v, \quad \&c. \end{aligned}\right\} \tag{464}$$

Hence (463) becomes

$$p = \left[\frac{m_1 p_1 \cdot \frac{v_1}{v}\,\delta v + m_2 p_2 \cdot \frac{v_2}{v}\,\delta v + \&c.}{m\delta v}\right]_{\tau_1, \tau_2, \&c.}$$

$$= \frac{m_1 p_1 v_1 + m_2 p_2 v_2 + \&c.}{mv}, \qquad (465)$$

which seems a reasonable rule for calculating the average pressure of the system. But in making use of this in investigations, it must be kept in mind that the variations of p are to be subject to the condition (464).

An *alternative, but equivalent*, mode of treatment has been suggested in Chapter XVI., which, more fully stated, is the following:—

At any given instant the volume and intrinsic energy of a body or system are quite definite and calculable (at least theoretically) from its given state at that instant, and its intrinsic energy would remain unaltered if it were permitted to settle into a state of uniform pressure and temperature without change of volume and without receiving or parting with any heat, but each particle being deprived of its visible kinetic energy at that instant. The body or system, having reached its settled state, would now have *a definite pressure, temperature, and entropy, which might be defined as the pressure, temperature, and entropy of the body or system at the given instant.*

Defined in this way, *the pressure, temperature, and entropy of a body or system will change continuously during an intrinsically irreversible transformation just as they would do during a reversible transformation in which the variations of volume and intrinsic energy are the same. Hence all the theorems which are true of the latter are also true of the former.*

Consequently, *in every cycle of transformations, whether*

reversible or irreversible, Thomson's or Clausius' theorem holds, namely:—

$$\int \frac{dH}{t} = 0, \tag{466}$$

where t is the absolute temperature of the body or system at which it receives the quantity of heat dH; and the integration extends over the cycle.

And the whole system of thermodynamic formulæ are applicable to any body or system subjected to any transformation or series of transformations whatever.

NOTE.—In (466), and in general, dH must include any accession or loss of heat due to transformation of the visible kinetic energy of the particles of the body into heat, or the reverse.

Exercises.

1. Prove that

$$J\left\{K\left(\frac{d}{dt}\right)_v \log\left[K\left(\frac{dt}{dv}\right)_p\right] - N\left(\frac{d}{dt}\right)_p \log\left[N\left(\frac{dt}{dp}\right)_v\right]\right\} = \left(\frac{dv}{dt}\right)_p \left(\frac{dp}{dt}\right)_v.$$

2. Prove that

$$\left(\frac{d}{dp}\right)_\phi \left[Ke^{-\int\mu dt}\left(\frac{dt}{d\phi}\right)_p\right] = 0.$$

3. Prove that

$$\left(\frac{d}{dv}\right)_\phi \left[Ne^{-\int\mu dt}\left(\frac{dt}{d\phi}\right)_v\right] = 0.$$

4. Prove that

$$\left(\frac{d}{dt}\right)_\phi \left[Me^{-\int\mu dt}\right] = 0.$$

5. Prove that

$$\left(\frac{d}{dp}\right)_t \left[Ke^{-\int\mu dt}\right] = \left(\frac{d}{dt}\right)_p \left[Me^{-\int\mu dt}\left(\frac{dv}{dp}\right)_t\right].$$

6. Prove that

$$\left(\frac{d}{dv}\right)_t \left[Ne^{-\int\mu dt}\right] = \left(\frac{d}{dt}\right)_v \left[Me^{-\int\mu dt}\right].$$

7. Prove that

$$\left(\frac{d}{dt}\right)_\phi \left[Me^{-\int\mu dt}\left(\frac{dv}{d\phi}\right)_t\right] = 0.$$

8. Prove that, if neither α nor $\beta = t$,

$$\left(\frac{d}{d\alpha}\right)_\beta \left[c_\alpha e^{-\int\mu dt}\left(\frac{dt}{d\beta}\right)_\alpha\right] = \left(\frac{d}{d\beta}\right)_\alpha \left[c_\beta e^{-\int\mu dt}\left(\frac{dt}{d\alpha}\right)_\beta\right].$$

9. Prove that, if t denote temperature on the constant-volume air thermometer (counted from absolute zero), and τ the corresponding expression for the temperature on the absolute scale, and if N is constant, or a function of t only,

$$\tau - t = \text{a constant, or zero.}$$

10. If $\psi = E + pv$, and K be constant, prove that

$$v = \frac{R\tau}{p} - \frac{1}{3}AJK\left(\frac{\tau_0}{\tau}\right)^2$$

and

$$\left(\frac{d\tau}{dp}\right)_\psi = A\left(\frac{\tau_0}{\tau}\right)^2$$

are inconsistent.

expand adiabatically to five times its original volume; it is then admitted to the condenser, and driven into it under a pressure of $3\frac{1}{2}$ lbs. per square inch. Calculate the work done per pound of steam used, supposing the volume of a pound of steam on admission to the cylinder to be $15\frac{1}{2}$ cubic feet.

24. In a high pressure expansion steam engine, steam of temperature 300° C. and of pressure 60 lbs. per square inch is admitted to the cylinder, and allowed to expand isothermally to four times its initial volume; it is then admitted to the condenser, and is driven into it under a pressure of 4 lbs. per square inch. Calculate the work done per pound of steam used, supposing the volume of a pound of steam on admission to the cylinder to be 10·25 cubic feet.

25. In a Siemen's "Regenerative Steam Engine" the steam is admitted to the cylinder at a temperature of 300° C. and pressure 60 lbs. per square inch, is allowed to expand isothermally to four times its original volume, and is then driven out under a pressure of 4 lbs. per square inch.

Compare the efficiency of this engine with that of a similar engine without a regenerator. Given that

$$J \,.\, H_t = 885200 + 423{\cdot}83\ (t - 100) \text{ ft. lbs.},$$

t denoting temperature counted from the freezing temperature.

INDEX.

[*The numbers refer to the pages.*]

Absolute scale of temperature, 81–87, 155, 167–168, 170.
Absolute scale of temperature, relation to scale of constant-pressure air-thermometer, 88–96.
Absolute temperature, *not* the reciprocal of Carnot's Function, 82–83.
Absolute zero of temperature, 84.
Aceton (C_5H_6O), vapour of, has negative specific heat, 128.
Adiabatic lines or isentropes, 39.
Air engine, Stirling's, 107–109.
Air, heat of compression of, 144, 166.
Air, properties of, 97–109.
Air, specific heats of, 97–99.
Air thermometer, relation of scale of constant-pressure air thermometer to the Absolute Scale, 88–96.
Author's formula for dry vapours, 113.
Available energy or motivity, 179.

Bacon, 16.
Bichloride of carbon vapour resembles vapour of water in having negative specific heat, 128.
Bisulphide of carbon vapour has negative specific heat, 128.
Boiling temperature of water raised by increase of pressure, 125.
Boyle, 16.
Boyle's Law of Gases, 97.

Caloric theory of heat, 16.
Capacity for heat of air or gases, 97–99.
Capacity for heat of water, 125.
Carbonic acid isothermals, 113.
Carnot's Axiom, 27.
Carnot's Cycle, 25, 31–33.
Carnot's Function, 37.
Carnot's heat engine, proof of perfection of, 34.
Chloroform vapour has negative specific heat, 128.
Clerk Maxwell's correction of Carnot's Cycle, 32.
Clausius' Axiom, 27.
Clausius' discovery about carbon bichloride, carbon bisulphide, chloroform, aceton, and ether, 128.
Clausius on condensation of steam during adiabatic expansion, 127–129.
Clausius' latent heat of water diminished by increase of pressure, 125.
Clausius' specific heat of water, 125.
Clausius' proof of Second Law, 125.
Coefficients, partial differential, 72–73.
Coefficients of elasticity, 74–80.
Coefficient of elasticity, constant temperature, 74.
Coefficient of elasticity, constant entropy, 75.
Coefficients of elasticity, ratio of, 76.
Coefficient of cubical expansion, 75.
Colding, 22.
Conditions of reversibility of heat engine, 26.
Criterion of perfection of heat engine, 26.
Curves, thermal, 38–39.
Cycles of operations, 30–33, 38, 39, 45, 51–52.
Cycles of operations, the (α, β) cycle, 40–43.
Cycles of operations, the (α, ϕ) cycle, 62.

Cycles of operations, the Isobarenergicycle, 38, 39, 58–59.
Cycles of operations, the Isobarentropicycle, 38, 39, 54.
Cycles of operations, the Isobarymegacycle, 38, 39, 56.
Cycles of operations, the Isobarythermocycle, 38, 39.
Cycles of operations, the Isenergimegacycle, 38, 40, 59–60.
Cycles of operations, the Isenergentropicycle, 38, 39, 57–58.
Cycles of operations, the Isentropimegacycle, 38, 39, 55.
Cycles of operations, the Isothermenergicycle, 38, 40, 60–61.
Cycles of operations, the Isothermentropicycle, 38, 39, 45, 51–52.
Cycles of operations, the Isothermomegacycle, 38, 39, 53.
Cycles of operations, the (t, β) cycle, 61–62.

Davy, Sir Humphry, 16.
Davy, Sir Humphry, proof of immateriality of heat, 19–21.
Density of water, maximum, 78–80.
Diagrams—thermographs, 38.
Diagrams—isographs, 38–40.
Diagrams—cycles, 39, 51–62.
Differential Coefficients, Partial, Table of, 72–73.
Dilatation, coefficient of, 75.
Dilatation, latent heat of, 51.
Dissipation of energy, 180.
Dissipation of energy, principle of, 186.
Duty of an engine, 107.
Dynamical theory of heat, 16–28.

Efficiency of perfect heat engine, 37.
Elasticity, coefficients of, 74–80.
Energy, available or motivity, 179.
Energy, dissipation of, 180, 186.
Energy, intrinsic, 39.
Engine, Carnot's, 30–33.
Engine, Siemen's regenerative steam, 120.
Engine, Stirling's regenerative air, 107–109.
Entropy, 39, 46, 187–194.
Equivalent of heat, dynamical, 22.
Equation of Isentrope, of mixture of steam and water, 131.
Equation of Isothermal of mixture of steam and water, 131.
Equation of Isenerg of mixture of steam and water, 133.
Ether, vapour of, has positive specific heat, 128.
Experiments, the Joule, 23.
Experiments, the Joule-Thomson, 91–96.
External work, 12–15.

Foot-pound of work, 8.
Foot-poundal of work, 8.
Formulæ—First Law, 24.
Formulæ—Second Law, 39.
Formulæ—Second Law, extension of, 47.
Formulæ—Isothermentropicycle, &c., 39, 51–62.
Formulæ—for mixtures of substance in two states, 122–149.
Formulæ—Table of Partial Differential Coefficients, 72–73.
Formulæ—coefficients of elasticity, 74–80.
Formulæ—coefficient of dilatation, 75.
Formulæ—relation of absolute scale and constant pressure air-thermometer scale, 88–96.
Formulæ—perfect gases, 97–109.
Formulæ—efficiency of Carnot's engine, 37.
Formulæ—latent heat, 122–149.
Formulæ—efficiency of Stirling's engine, 107–109.
Formulæ—for dry vapours, 110–121.
Formulæ—work of steam expanding adiabatically, 117–118.
Formulæ—expanding isothermally, 119–120.
Formulæ—work of Sieman's regenerative engine, 120.
Formulæ—of transformation, 3.
Formulæ—usual method of obtaining, 150–172.
Freezing temperature lowered by increase of pressure, proved by Prof. James Thomson, 124.

Gases, perfect, 97–109.
Gases, thermoelastic laws of, 97.
Gases, Boyle's law, or isothermal, 97.
Gases, Charles' law, or isobaryc, 97.
Gases, general formula, 97.

Gases, adiabatic or isentropic laws, 99–101.
Gases, specific heats of, 97–99.
Gases, coefficients of elasticity of, 74–80.
Gases, latent heat of dilatation of, *M*, 51.
Gases, coefficient of dilatation of, *e*, 75.
Gases, velocity of sound in kinetic theory of, 20–21.
Gases, formulæ for, 97–109, 171–172.
Gases, specific heat, pressure constant, 52–53, 98–109.
Gases, specific heat, volume constant, 53, 98–109.
Geometrical representation of work, 6.
Geometrical proof of transformation formulæ, 4.

Heat, a form of energy (Davy, Rumford), 16–24.
Heat, capacity for, of water, 125; of gases, 97–99.
Heat engine, Carnot's, 30–33.
Heat engine, Stirling's, 107–109.
Heat, dynamical equivalent of (Joule), 22.
Heat, latent, 122–149.
Heat, latent, of liquefaction of ice, 125.
Heat, latent, of evaporation of water, 125–126.
Heat, latent, of dilatation, 51.
Heat, specific, of gas under constant pressure, 97–108.
Heat, specific, of gas under constant volume, 97–109.
Heat developed by compression of gases, 104, 166.
Hirn's formula for dry vapours, 111.

Ice, effect of pressure on the melting point of, 19.
Irreversibility, conditional, 173–4.
Irreversibility, intrinsic, 174.
Isograms, 38–39.
Isobaryc lines, 39.
Isodiabatic lines, 39.
Isenergic lines, 39, 103, 133.
Isentropic lines, 39, 46, 131.
Isomegal lines, 39.
Isothermal lines, 39, 131, 132.
Isographs, 38.
Isoalphabetacycle, 40–43.
Isobarentropicycle, 38, 39, 54.
Isobarymegacycle, 38, 39, 56.
Isobarythermocycle, 38, 39, 52–53.
Isobarenergicycle, 38, 39, 58–59.
Isentropimegacycle, 38, 39, 55.
Isenergentropicycle, 38, 39, 57–58.
Isothermentropicycle, 38, 39, 45, 51–52.
Isothermomegacycle, 38, 39, 53.
Isonergimegacycle, 38, 40, 59–60.
Isothermenergicycle, 38, 40, 60–61.

Joule, 22.
Joule, dynamical equivalent, 22.
Joule, experiment on free expansion of air, 23.
Joule-Thomson, experiments on the flow of gases through porous plugs, 91–96.

Kinetic theory of gases, 21–22.

Latent heat, 122–149.
Latent heat of fusion or liquefaction of ice, 125.
Latent heat of evaporation of water, 126.
Latent heat of water diminished by increase of pressure, 125.
Latent heat of steam, 125; diminished by increase of pressure, 126.
Latent heat of dilatation, 51.
Law, Boyle's, 97.
Law, Charles', 97.
Laws of Thermodynamics, 29–37.
Laws of Thermodynamics, First Law—Rumford, Davy, 29, 16, 45, 42, 152; Joule, 22.
Laws of Thermodynamics, Second Law—Carnot, Clausius, 25, 45, 49–50, 152; Thomson, 24; extension of, 46–50; Thomson's or Clausius', 47.
Lines—thermal, or thermograms, 38–39.
Lines—isobars, 39.
Lines—isonergs, 39.
Lines—isentropes, or adiabatics, 39.
Lines—isomegs, 39.
Lines—isotherms, 39.
Lines—constant vapour-mass, 132.

Liquefaction of steam by expansion, 127, 129.
Locke, 16.
Lowering of the freezing temperature by increase of pressure, 124.

Maximum density of water, 78–80.
Maxwell, Clerk—correction of Carnot's cycle, 32.
Maxwell Clerk—on solid and liquid states, 126–127.
Mayer, 22.
Mayer's hypothesis, 22, 105, 167.
Mayer's hypothesis, confirmed by the Joule and the Joule-Thomson experiment, 23–24, 91–96, 167.
Mechanical equivalent of heat, 18, 22, 24.
Mechanical equivalent of heat—Rumford, Davy, Mohr, Seguin, Mayer, Colding, Joule, 16–24.
Melting point, influence of pressure on, 124.
Mixture of solids and liquids, 124.
Mixture of liquids and gases, 125.
Molecular motion, 20–21.
Mohr, 22.
Motivity, or available energy, 179.
Motivity, internal thermodynamic, 184.
Motivity, external, 182.
Motivity and dissipation, 179–186.

Newton's theoretical velocity of sound, 103.

Operations, cycle of, Carnot's, 38, 39, 45, 51–52.
Operations, cycle of, Isobarentropicycle, 38, 39, 54.
Operations, cycle of, Isobarymegacycle, 38, 39, 56.
Operations, cycle of, Isobarythermocycle, 38, 39, 52–53.
Operations, cycle of, Isobarenergicycle, 38, 39, 58–59.
Operations, cycle of, Isentropimegacycle, 38, 39, 55.
Operations, cycle of, Isenergentropicycle, 38, 39, 57–58.
Operations, cycle of, Isothermentropicycle, 38, 39, 45, 51–52.
Operations, cycle of, Isothermomegacycle, 38, 39, 53.
Operations, cycle of, Isothermenergicycle, 38, 40, 60–61.
Operations, cycle of, Isenergimegacycle, 38, 40, 59–60.

Partial Differential Coefficients, Table of, 72–73.
Perfect heat engine, reversible, 26.
Pressure, influence of pressure on the melting point of ice, 124.
Pressure, laws connecting pressure and volume, pressure and temperature, &c., of gases, 97–109.
Properties of gases, 97–109.
Properties of vapours in contact with their liquids, 122–149.
Properties of vapours not in contact with their liquids, 110–121.

Rankine, First Law of Thermodynamics, 24.
Rankine, molecular vortices, 28.
Rankine discovers that the specific heat of steam is negative, 125.
Rankine, law connecting pressure and volume of dry saturated steam, 142.
Rankine's formula for dry vapours, 110.
Regnault, 88, 89.
Reversible cycle of operations, 25.
Reversibility, the criterion of perfection of a heat engine, 26.
Reversibility and irreversibility, 173–178.
Reversibility of operation, 173.
Reversibility of operation, conditions of, 26, 175.
Ritter's formula for dry vapours, 111.
Rumford on immateriality of heat, 16–19.

Scale of temperature, air thermometer, 90.
Scale of temperature, absolute, 81–87.
Scale of temperature, relation between absolute scale and scale of constant-pressure air thermometer, 88–95.
Specific heat of gases, pressure constant, *K*, 97–99.
Specific heat of gases, volume constant, *N*, 97–99.

Specific heat of steam or vapour of water negative, 125–129.
Specific heat of water, 125.
Steam, adiabatic expansion of, 117–118.
Steam, isothermal expansion of, 119–120.
Steam, Rankine's formula for work done in a stroke of piston of steam engine when the expansion is adiabatic, 135–136.
Steam, Rankine's formula for the work done in a double stroke on one face of piston when the steam expands isothermally, 119–120.
Steam, latent heat of, 125, 126; diminution of by increase of pressure, 126.
Steam, saturated, 140.
Steam and water, 135–144.
Steam, dry or superheated, 110–121.
Stirling's air engine, 107–109.

Table of Partial Differential Coefficients, 72–73.
Tait, criterion of reversibility, 48.
Temperature, absolute scale of, 81–87.
Temperature, absolute zero, 84.
Temperature, air thermometer, scale of, 88–95.
Temperature, critical, 112.
Thermal lines and cyclic diagrams, 38–45.
Thermodynamics, laws of, 29–37.
Thermodynamics, history of, 16–28.
Thermograph, 38.
Thermogram, 38.
Thomson, James, correction of Carnot's cycle of operations, 32.
Thomson, James, effect of pressure on melting point of ice, 124.
Thomson, James, theory of isothermals, 111.
Thomson, James, solid and liquid states, 127.
Thomson, Sir William (Lord Kelvin), First Law of Thermodynamics, 24.
Thomson, absolute scale of temperature, 81–87.
Thomson, Second Law of Thermodynamics, 25.
Thomson and Joule's experiments on the flow of gases through plugs, 91–96.
Thomson, on motivity, 179–186.
Thomson, raising and lowering of melting point of ice by pressure, 127.
Thomson, axiom, 27.
Thomson, extension of Second Law, 47.
Thomson, proof of Second Law, 36.
Thomson, formula for dry vapours, 110.
Thomson, on the specific heat of steam, 127–128.
Transformation, reversible, 173.
Transformation, irreversible, conditionally, 174.
Transformation, irreversible, intrinsically, 174.
Transformation, irreversible, treatment of, 187–194.

Water, latent heat of, diminished by increase of pressure, 125.
Water, specific heat of (Regnault), 125.
Water and ice, 145–149.
Work, definition of, 6.
Work, measurement of, 6.
Work, units of, 7, 8.
Work, geometrical representation of, 9–15.
Work, of high pressure steam expanding adiabatically, 117–118.
Work, of dry vapour in Carnot's cycle, 116.
Work, of high pressure steam expanding isothermally, 119–120.
Work, of Siemen's regenerative steam engine, 120.
Work expended in compressing gases, 166–167.

Zero, absolute, 84.
Zeuner's formula for dry vapours, 111.

THE END.

Printed at THE UNIVERSITY PRESS, *Dublin*.